

Supporting Information

Ethanol Conversion on Cyclic (MO₃)₃ (M = Mo, W) Clusters

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Potential energy surfaces

The potential energy surfaces (PES, energies at 0K in kcal/mol) for the D₂O loss reactions, dehydration reactions, dehydrogenation reactions and H/D exchange reactions for ethanol regeneration are shown in Figures S3 to S13.

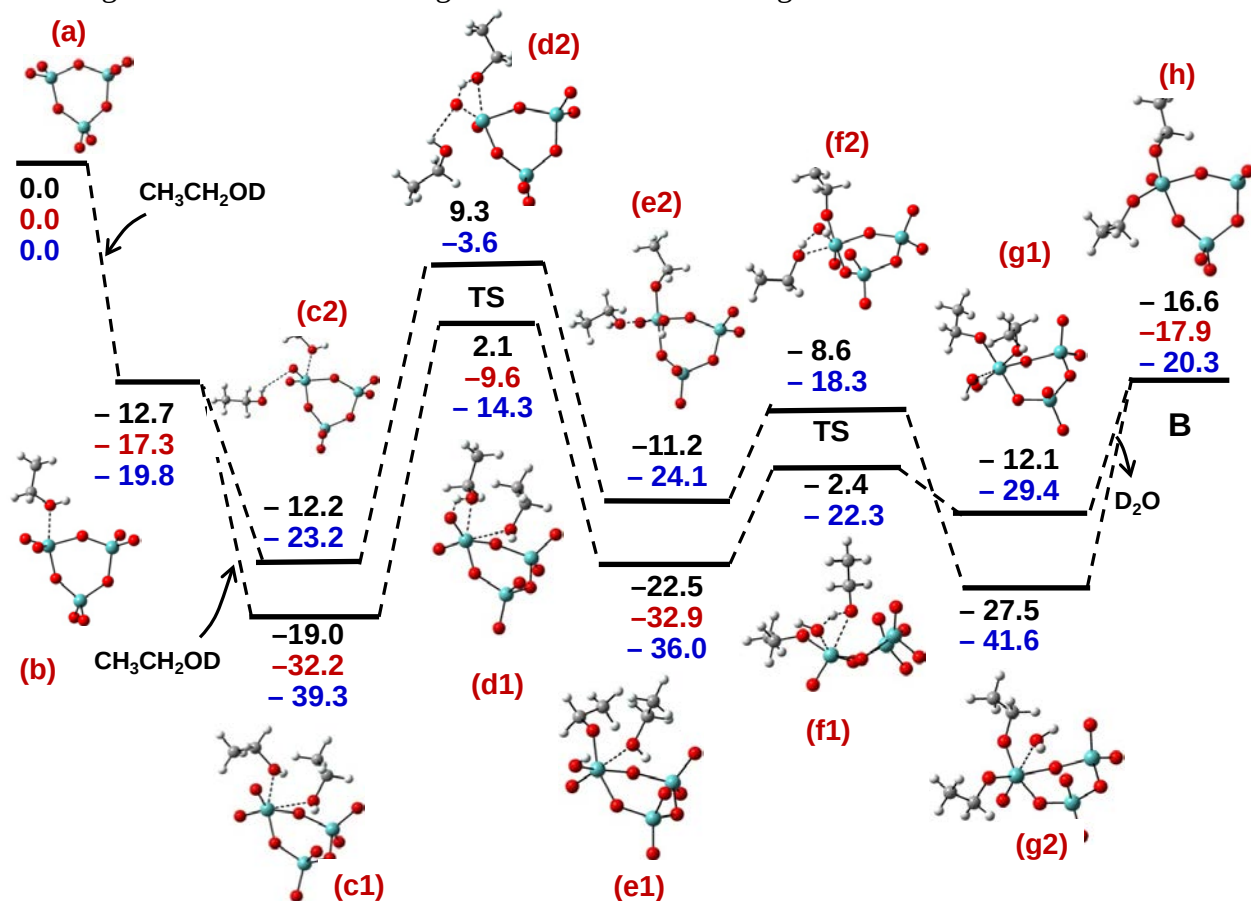


Figure S1. DFT with the B3LYP and M06 functionals and CCSD(T) potential energy surfaces in kcal/mol for the elimination of D₂O from the reaction of 2C₂H₅OD + (MoO₃)₃. Reaction pathway 1 is identical with the PES for M = Mo in Figure 3 in manuscript. ΔE Energies in black = B3LYP/ aug-cc-pVDZ-PP (aD), in crimson = M06/aD//B3LYP/aD and in blue = CCSD(T)/aD//B3LYP/aD. Atoms, Mo = light blue, O = red, C = grey, and H = white.

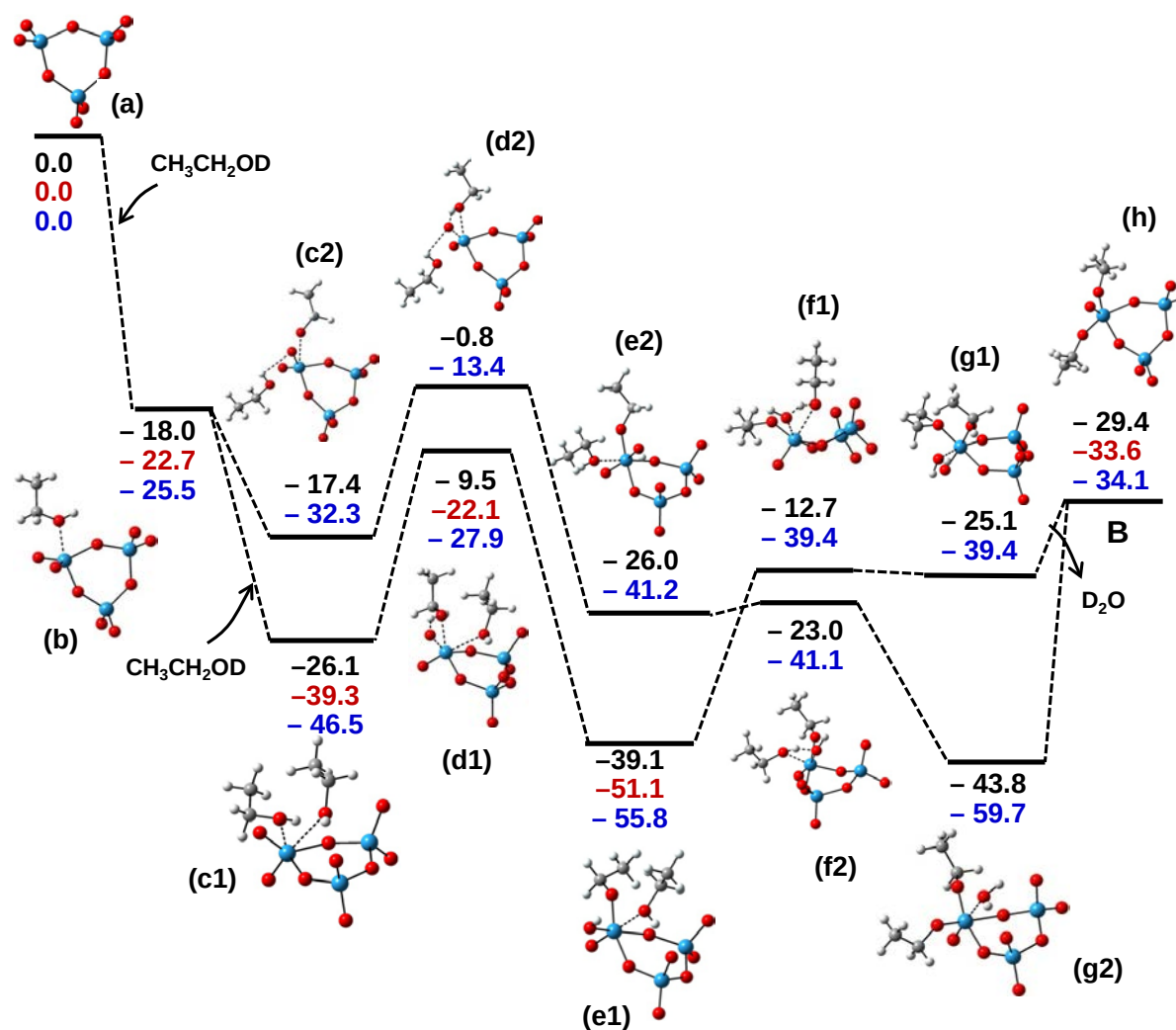


Figure S2. DFT with the B3LYP and M06 functionals and CCSD(T) potential energy surfaces in kcal/mol for the elimination of D_2O from the reaction of $2C_2H_5OD + (WO_3)_3$. Reaction pathway L is identical with the PES for $M = W$ in Figure 3 in manuscript. ΔE Energies in black = B3LYP/ aug-cc-pVDZ-PP (aD), in crimson = m06/aD//B3LYP/aD and in blue = CCSD(T)/aD//B3LYP/aD. Atoms, W = dark blue, O = red, C = grey, and H = white.

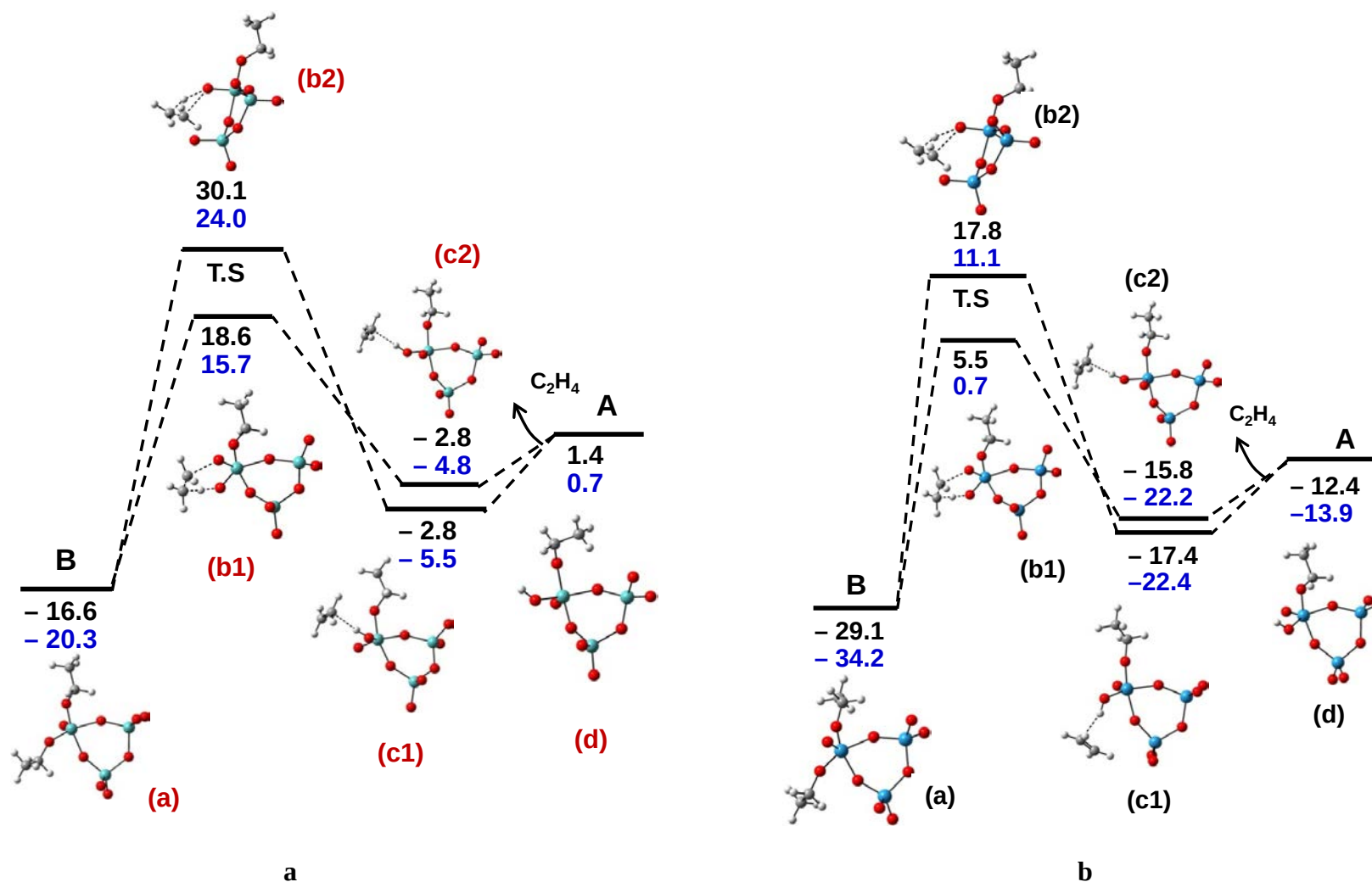


Figure S3. DFT with the B3LYP functional and CCSD(T) potential energy surfaces in kcal/mol for the formation of C_2H_4 (dehydration) and the precursor state (A) from the intermediate B of the reaction of $2C_2H_5OD + (MO_3)_3$. $M = Mo$ is shown in Figure S5a and $M = W$ is shown in Figure S5b. Reaction pathway 1 is identical with the PES in Figure 4 in manuscript. See Figure S3 and S4 legends.

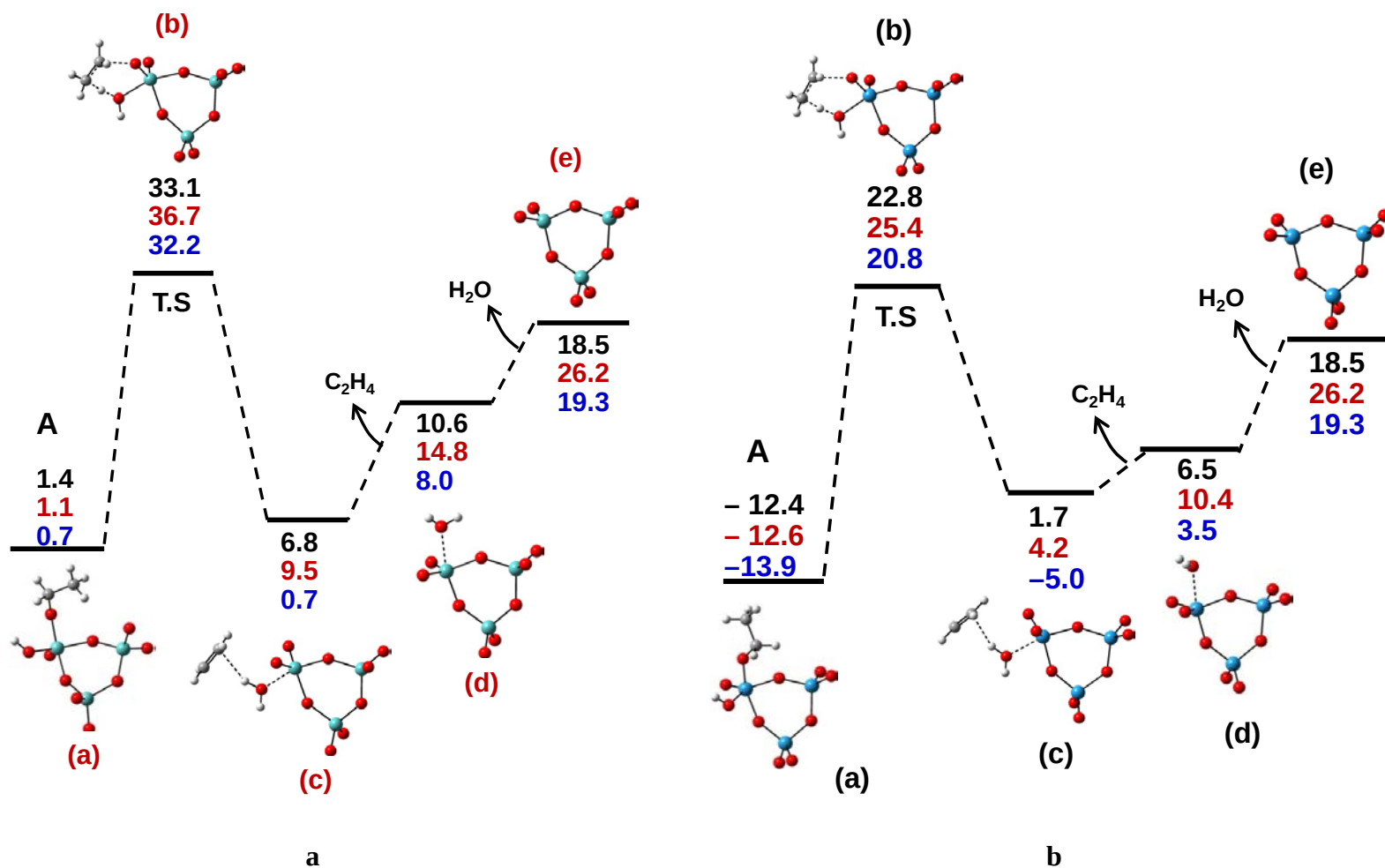


Figure S4. DFT with the B3LYP and M06 functionals and CCSD(T) potential energy surfaces in kcal/mol for the formation of H₂O and the second C₂H₄ (dehydration) from the intermediate A of the reaction of 2C₂H₅OD + (MO₃)₃. M= Mo is shown in Figure S6a and M = W is shown in Figure S6b. This reaction completes the catalytic cycle. Note that the overall catalytic process is endothermic. The dehydration reaction, 2CH₃CH₂OH → 2C₂H₄ + 2H₂O, is endothermic by 21.6 kcal/mol from experiment (at 298K)and 19.3 kcal/mol at the CCSD(T)/aD//B3LYP/aD level for the release of two C₂H₄ molecule. See Figure S3 and S4 legends.

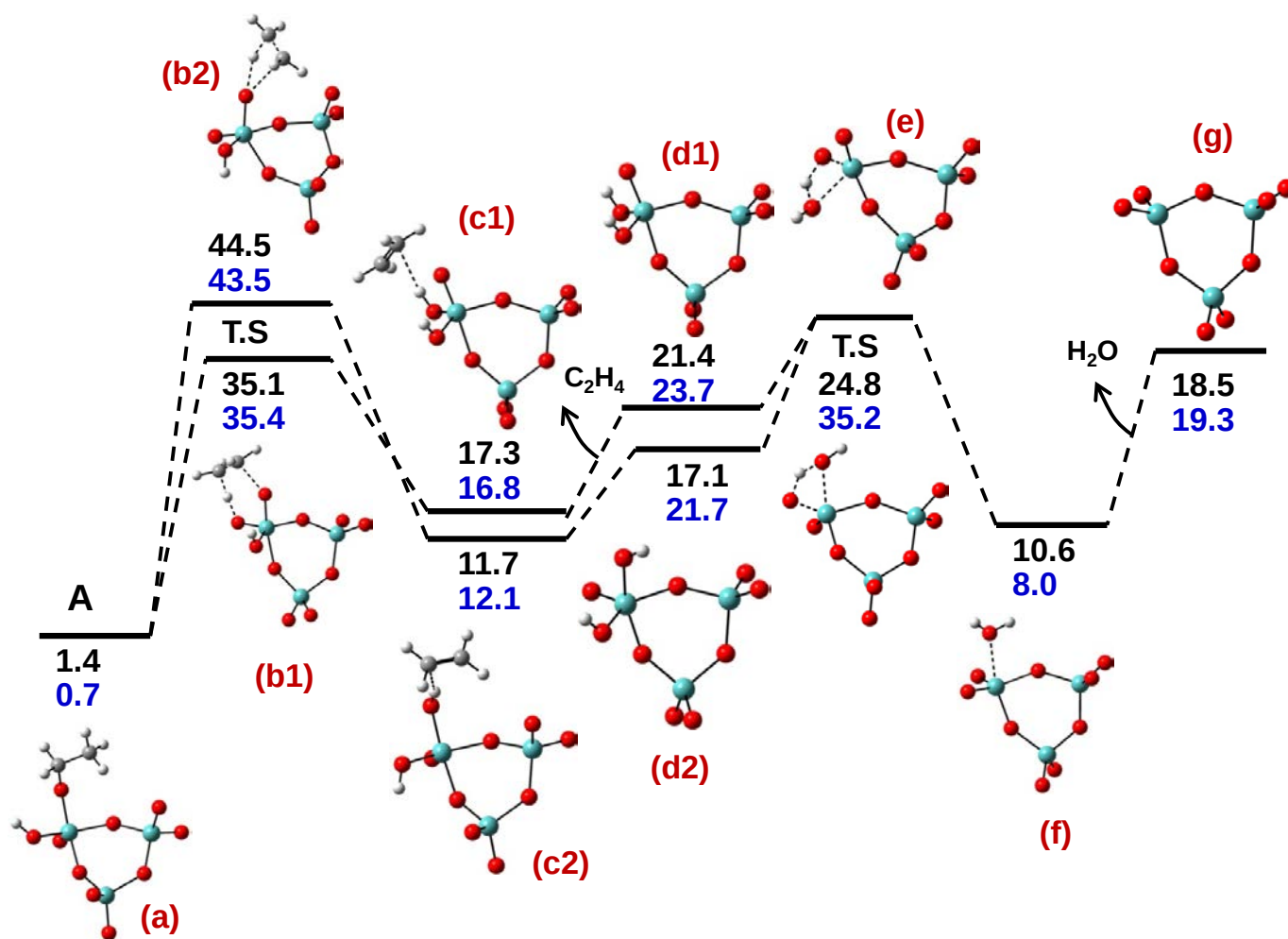


Figure S5. DFT with the B3LYP functional and CCSD(T) potential energy surfaces of the alternative pathway in kcal/mol for the formation of H₂O and the second C₂H₄ (dehydration) from the intermediate A of the reaction of 2C₂H₅OD + (MoO₃)₃. Completes the catalytic cycle. Note that the overall catalytic process is endothermic. This reaction completes the catalytic cycle. See Figure S3 legend.

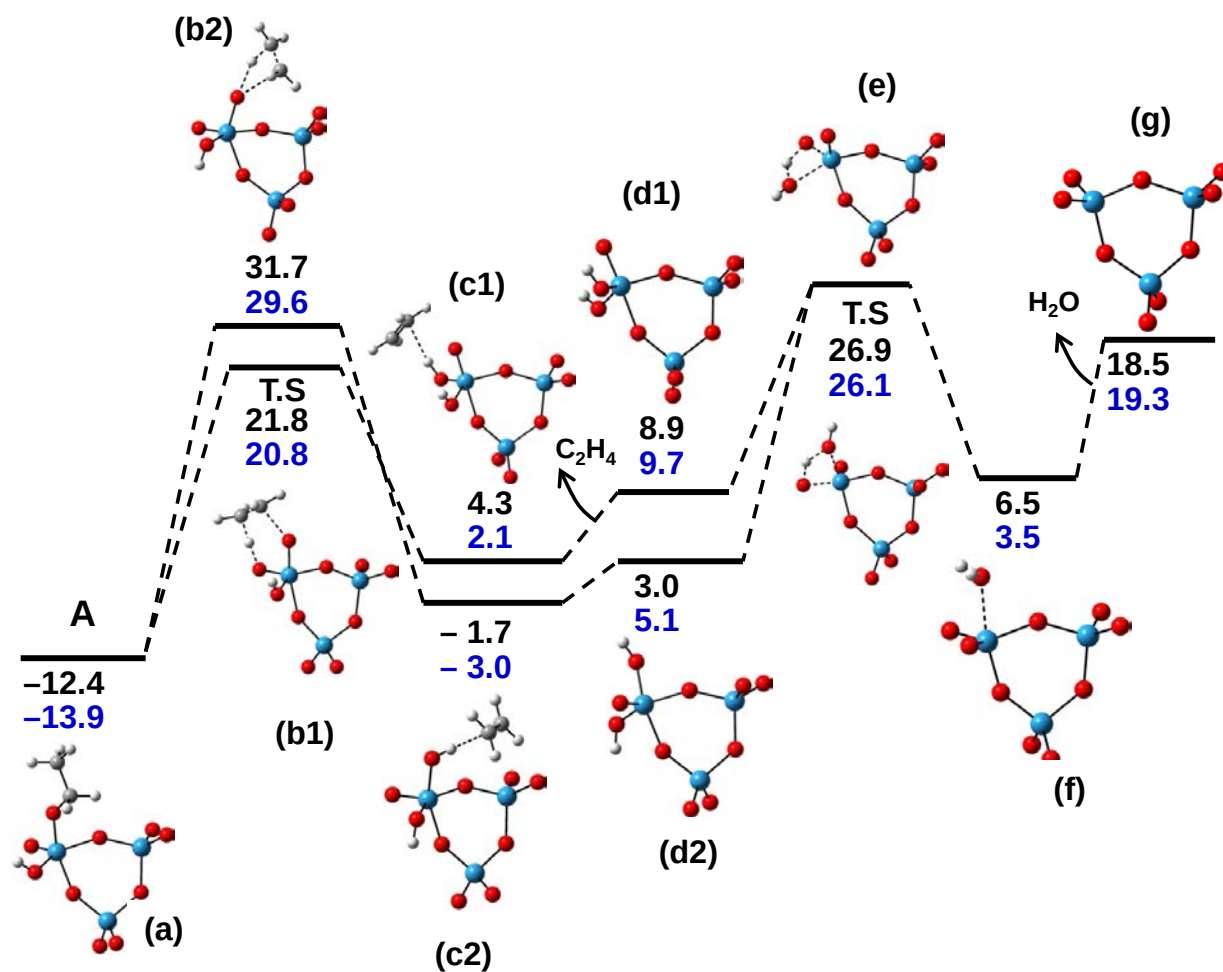


Figure S6. DFT with the B3LYP functional and CCSD(T) potential energy surfaces of the alternative pathway in kcal/mol for the formation of H_2O and the second C_2H_4 (dehydration) from the intermediate A of the reaction of $C_2H_5OD + (WO_3)_3$. Note that the overall catalytic process is endothermic. This reaction completes the catalytic cycle. See Figure S4 legend.

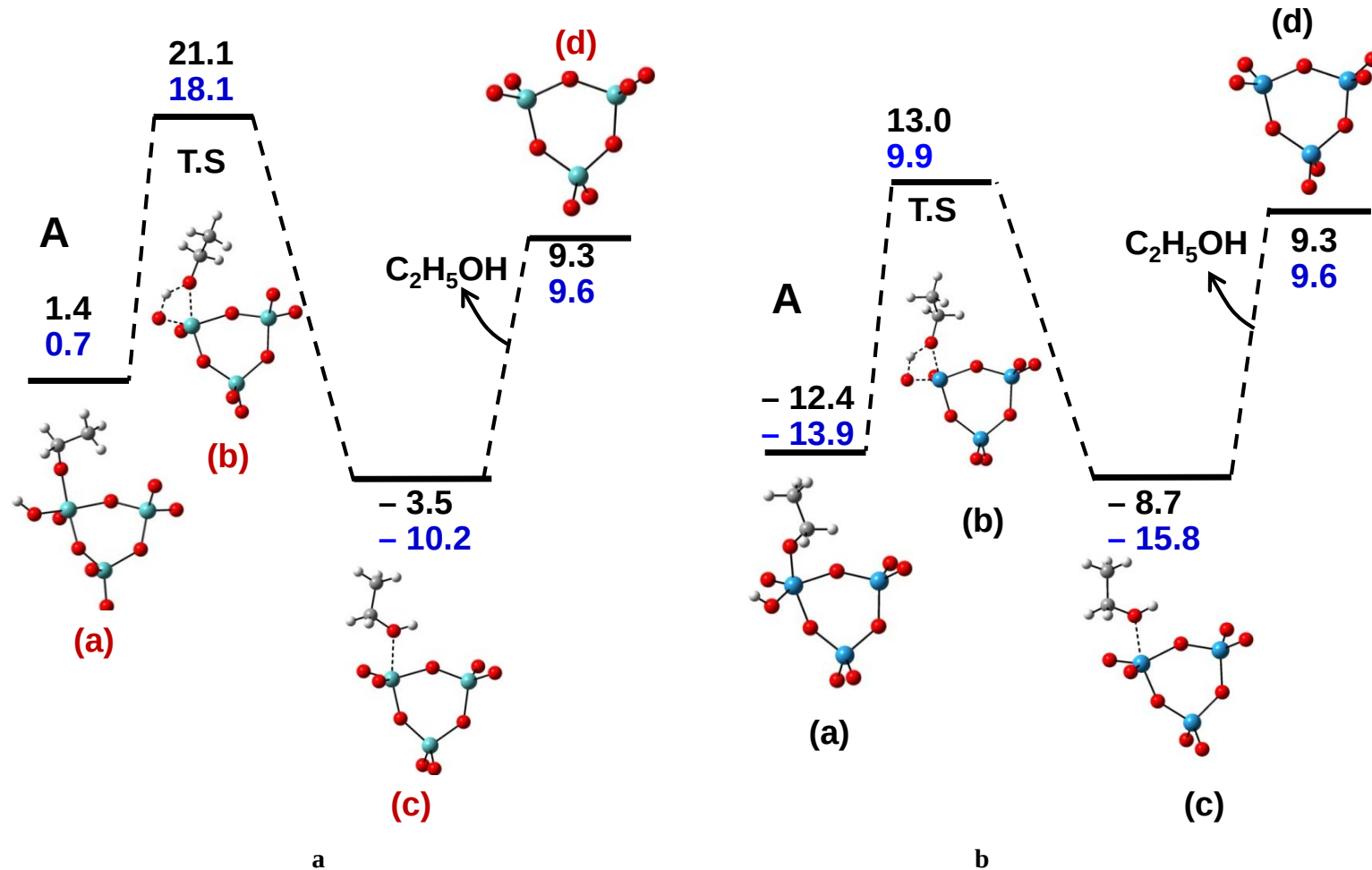


Figure S7. DFT with the B3LYP functional and CCSD(T) potential energy surfaces in kcal/mol for the H/D exchange reaction for ethanol regeneration from the intermediate A of the reaction of C₂H₅OD + (MO₃)₃. M= Mo is shown in Figure S9a and M = W is shown in Figure S9b. Note that the overall catalytic process is endothermic. See Figure S3 and S4 legends. This reaction completes the catalytic cycle.

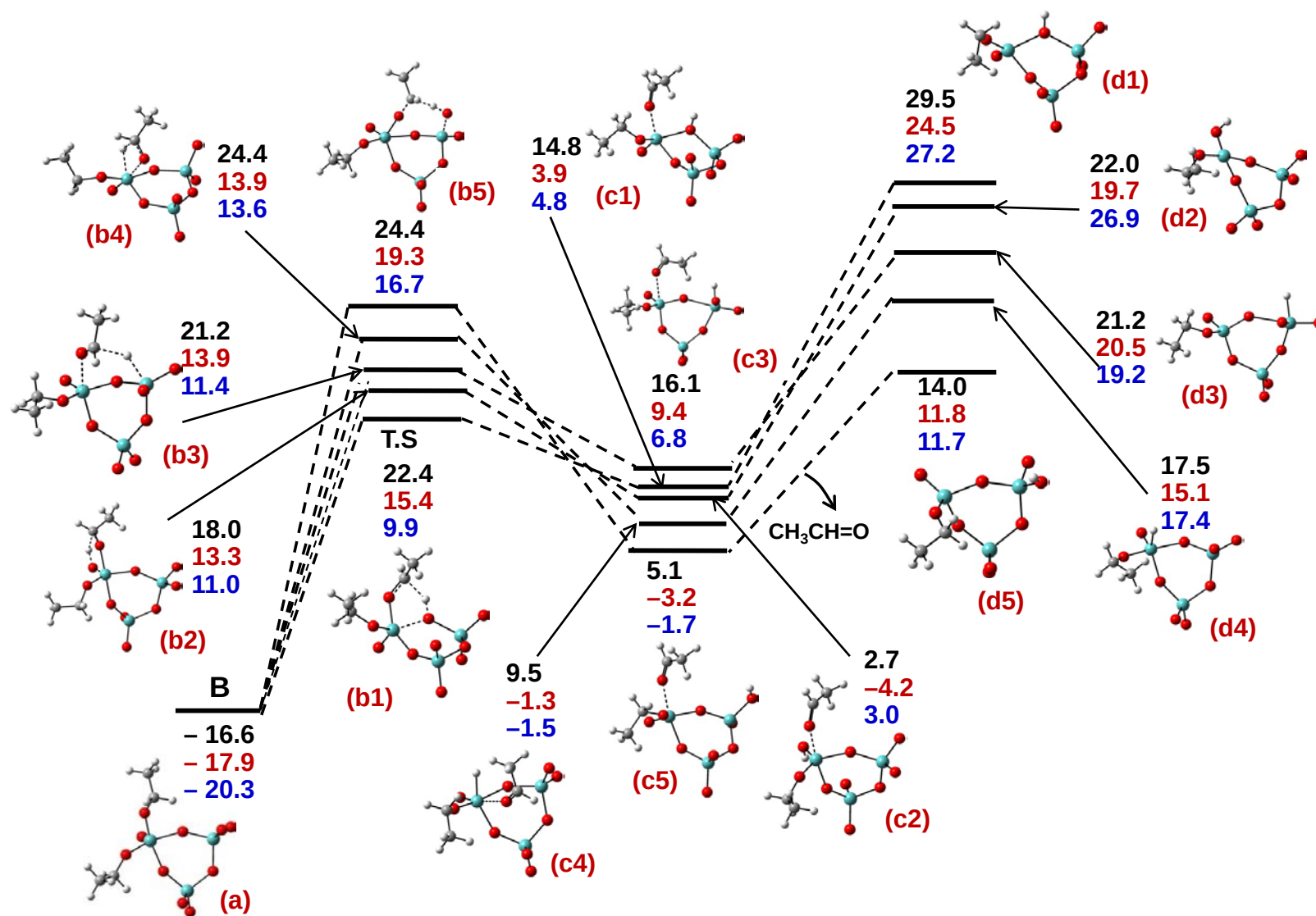


Figure S8. DFT with the B3LYP and M06 functionals and CCSD(T) potential energy surfaces in kcal/mol for the formation of $\text{CH}_3\text{CH}=\text{O}$ (dehydrogenation) from the intermediate B of the reaction of $\text{C}_2\text{H}_5\text{OD} + (\text{MoO}_3)_3$. Reaction pathways 1 and 5 are identical with the PESs for $\text{M} = \text{Mo}$ in Figure 5 in manuscript. See Figure S3 legend.

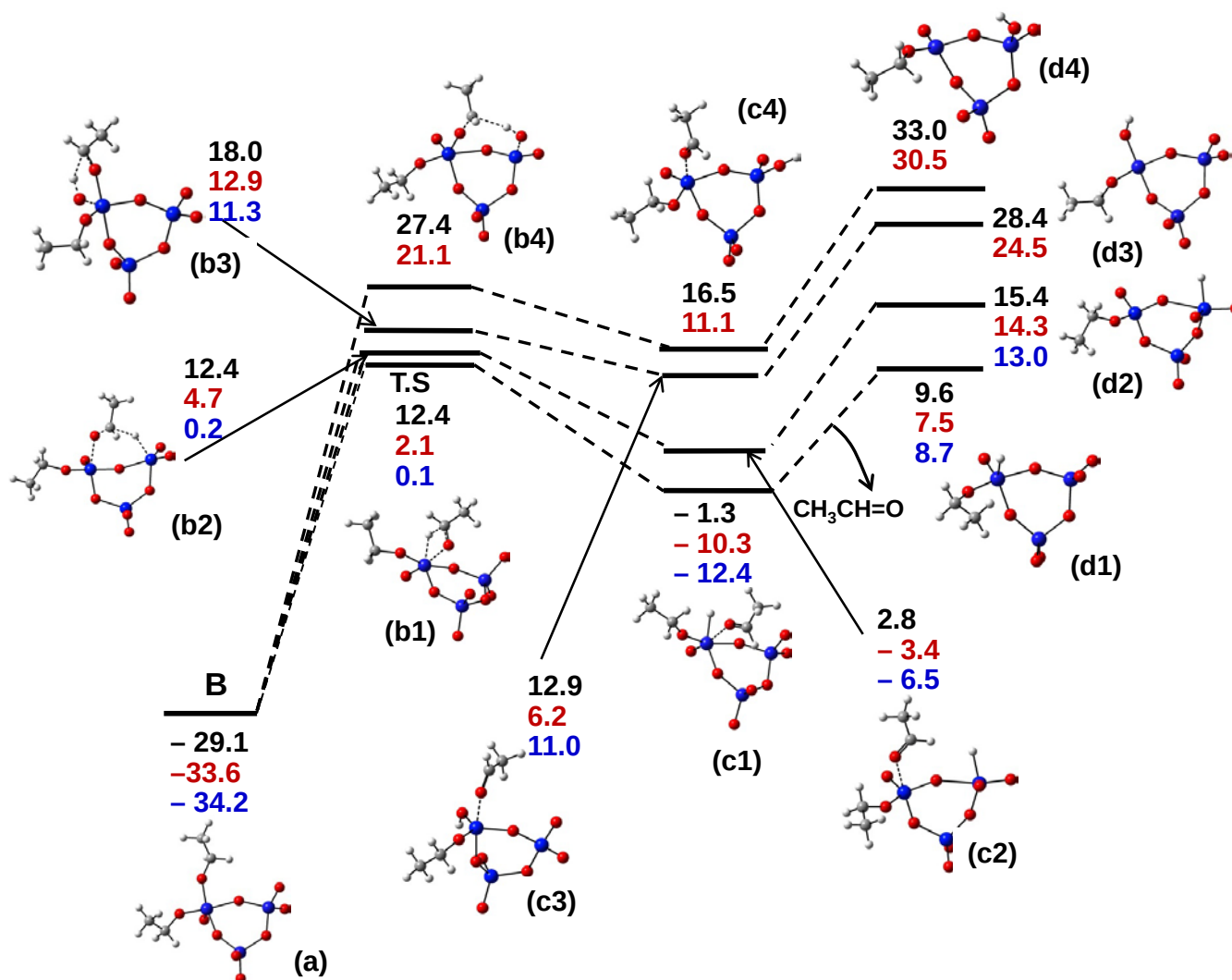


Figure S9. DFT with the B3LYP and M06 functionals and CCSD(T) potential energy surfaces in kcal/mol for the formation of $\text{CH}_3\text{CH}=\text{O}$ from the intermediate B of the reaction of $\text{C}_2\text{H}_5\text{OD} + (\text{WO}_3)_3$. Reaction pathway 1 is identical with the PES for $\text{M} = \text{W}$ in Figure 5 in manuscript. See Figure S4 legend.

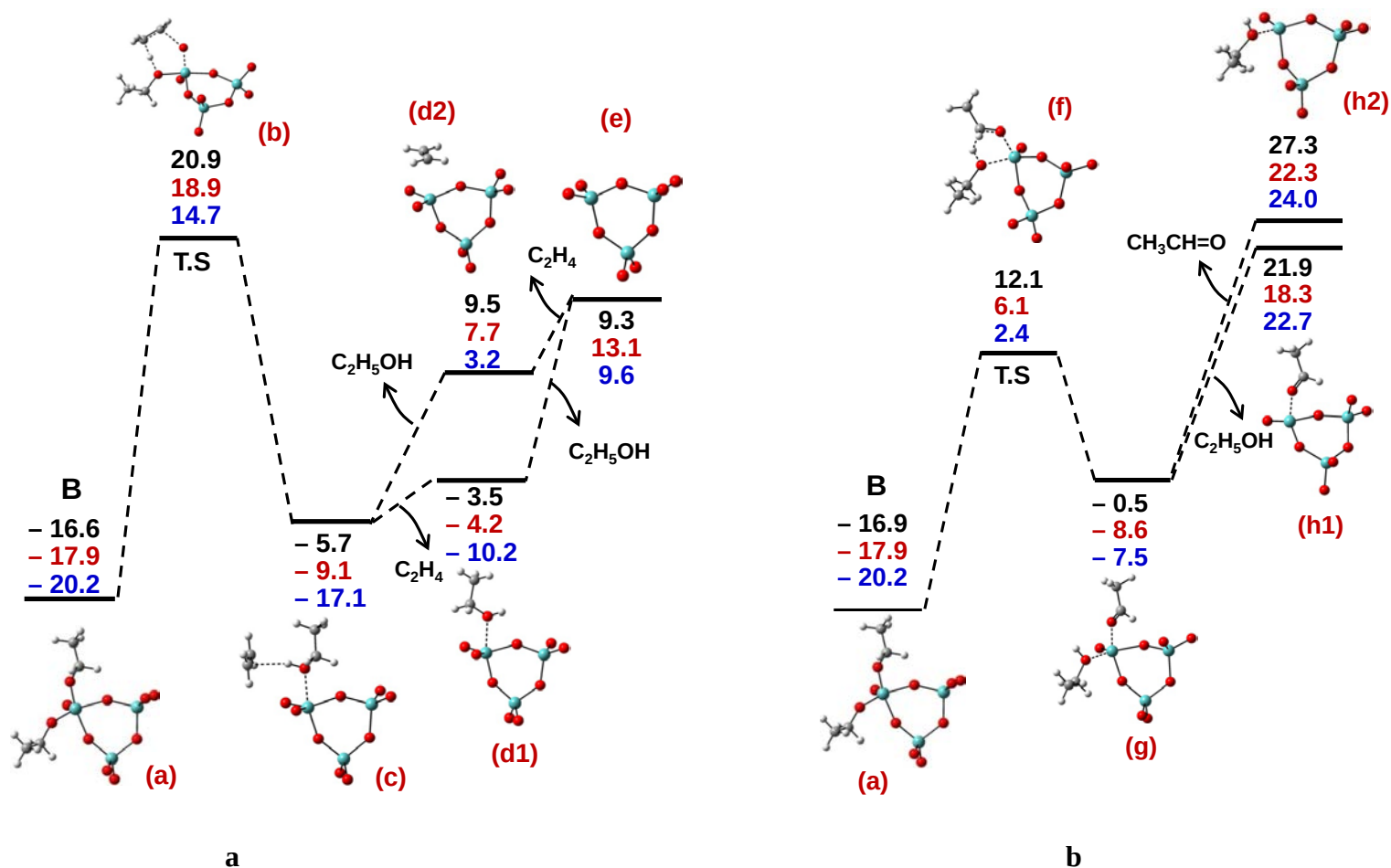


Figure S10. DFT with the B3LYP and M06 functionals and CCSD(T) potential energy surfaces in kcal/mol for the H/D exchange reaction for ethanol regeneration from the intermediate B of the reaction of $\text{C}_2\text{H}_5\text{OD} + (\text{MoO}_3)_3$. β hydrogen transfer to $\text{Mo}-\text{OCH}_2\text{CH}_3$ to regenerate $\text{CH}_3\text{CH}_2\text{OH}$ is shown in Figure S12a and α hydrogen transfer to $\text{Mo}-\text{OCH}_2\text{CH}_3$ to regenerate $\text{CH}_3\text{CH}_2\text{OH}$ is shown in Figure S12b. See Figure S3 legend. The reaction in Figure S12a completes the catalytic cycle. The dehydration reaction, $\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$, is endothermic by 10.8 kcal/mol from experiment (at 298K) and 9.6 kcal/mol at the CCSD(T)/aD//B3LYP/aD level.

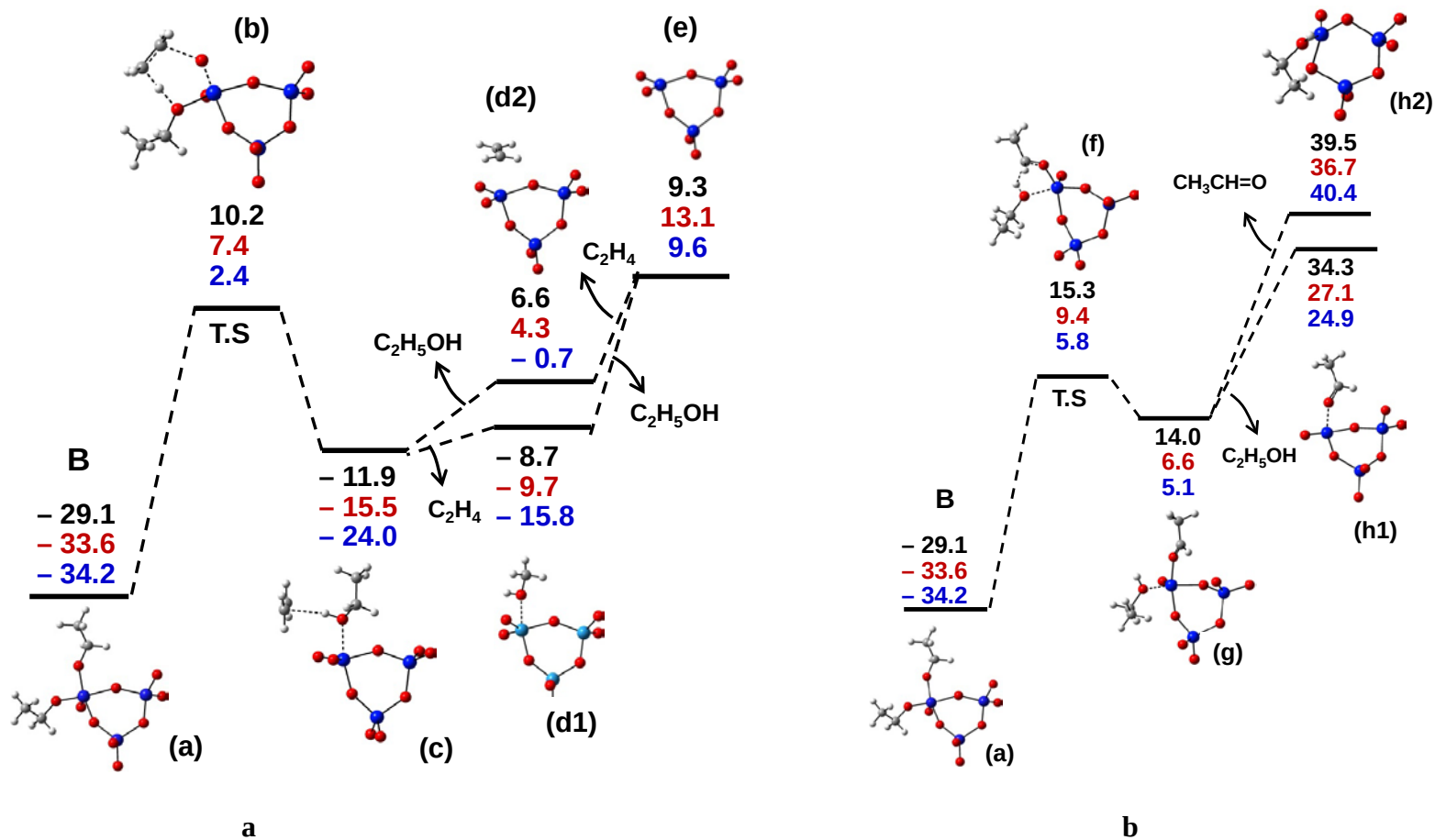


Figure S11. DFT with the B3LYP and M06 functionals and CCSD(T) potential energy surfaces in kcal/mol for the H/D exchange reaction for ethanol regeneration from the intermediate B of the reaction of $\text{C}_2\text{H}_5\text{OD} + (\text{WO}_3)_3$. β hydrogen transfer to $\text{W}-\text{OCH}_2\text{CH}_3$ to regenerate $\text{CH}_3\text{CH}_2\text{OH}$ is shown in Figure S13a and α hydrogen transfer to $\text{W}-\text{OCH}_2\text{CH}_3$ to regenerate $\text{CH}_3\text{CH}_2\text{OH}$ is shown in Figure S13b. See Figure S4 legend. The reaction in Figure S13a completes the catalytic cycle.

Table SI-1. Cartesian x,y,z Coordinates in Å for Optimized Geometries, Zero Point Energies (ZPE, a.u.) and Electronic Energies at 0 K ($E_{B,0K}$, a.u.) at the B3LYP/ aug-cc-pVDZ-PP (aD) Level. Single Point Electronic Energies at 0 K ($E_{m,0K}$, a.u.) at the M06/aD//B3LYP/aD and CCSD(T)/aD//B3LYP/aD Levels.

C₂H₅OH ZPE=0.079398 $E_{B,0K}$ =-155.0650856 $E_{m,0K}$ =-154.9545058 $E_{C,0K}$ =-154.6657354

C	1.224010	-0.224406	0.000007
C	-0.080617	0.551304	0.000011
H	2.078258	0.467443	0.000003
H	1.292666	-0.863689	0.890737
H	1.292656	-0.863683	-0.890728
H	-0.141176	1.197961	0.892712
H	-0.141150	1.198004	-0.892661
O	-1.155940	-0.397030	-0.000031
H	-1.994087	0.078813	0.000075

CH₃CH=O ZPE=0.054974 $E_{B,0K}$ =-153.853211 $E_{m,0K}$ =-153.747735 $E_{C,0K}$ =-153.4624191

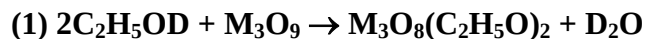
C	-0.231462	0.398687	-0.000002
C	1.169175	-0.150061	0.000001
H	1.160975	-1.245933	-0.000091
H	1.708584	0.227874	-0.882972
H	1.708530	0.227737	0.883064
O	-1.237055	-0.276932	0.000001
H	-0.307928	1.514027	-0.000004

C₂H₄ ZPE=0.050855 $E_{B,0K}$ =-78.598363 $E_{m,0K}$ =-78.519575 $E_{C,0K}$ =-78.36915648

C	0.667587	0.000000	0.000003
C	-0.667587	0.000000	-0.000004
H	1.241155	0.928249	-0.000009
H	1.241154	-0.928250	0.000024
H	-1.241155	-0.928249	0.000011
H	-1.241154	0.928250	-0.000022

H₂O ZPE=0.021228 $E_{B,0K}$ =-76.444643 $E_{m,0K}$ =-76.406755 $E_{C,0K}$ =-76.2739037

O	0.000000	0.000000	0.116954
H	0.000000	0.769997	-0.467816
H	0.000000	-0.769997	-0.467816



For M=Mo (Figure S3)

Mo₃O₉ (a) ZPE=0.031258 E_{B,0K}=-881.642362 E_{m,0K}=-881.164222 E_{C,0K}=-878.7210761

MO	0.000000	1.766326	-1.019778
MO	0.000000	-1.766326	-1.019778
MO	0.000000	0.000000	2.039589
O	-1.364399	2.628780	-1.517716
O	1.364399	2.628780	-1.517716
O	0.000000	0.000000	-1.724923
O	0.000000	1.493836	0.862478
O	1.364399	-2.628780	-1.517716
O	-1.364399	-2.628780	-1.517716
O	-1.364499	0.000000	3.035328
O	0.000000	-1.493836	0.862478
O	1.364499	0.000000	3.035328

Mo₃O₉·C₂H₅OH (b)

ZPE=0.112948 E_{B,0K}=-1036.730044 E_{m,0K}=-1036.148546 E_{C,0K}=-1033.420663

MO	0.714207	2.031548	-0.007232
MO	2.307475	-1.049091	0.030346
MO	-1.321761	-1.003274	-0.065257
O	0.717072	2.965045	-1.422640
O	0.700697	3.087421	1.319778
O	2.205515	0.849172	0.044627
O	-0.775577	0.899103	0.042082
O	2.986805	-1.635643	1.466597
O	3.242802	-1.616334	-1.262012
O	-2.010045	-1.740565	-1.426571
O	0.507937	-1.570080	-0.143301
O	-1.921222	-1.765465	1.325778
O	-3.219413	0.220409	-0.065770
H	-3.096979	1.046882	0.423276
C	-4.522423	-0.375798	0.225670
H	-4.600897	-1.206058	-0.483010
H	-4.494516	-0.781630	1.245441
C	-5.630007	0.641713	0.036365
H	-6.597368	0.161151	0.236592
H	-5.527963	1.483792	0.736819
H	-5.640933	1.030164	-0.989866

Pathway 1

Mo₃O₉·C₂H₅OH·C₂H₅OH (c1)

ZPE=0.196348 E_{B,0K}=-1191.809135 E_{m,0K}=-1191.130763 E_{C,0K}=-1188.121492

MO	0.926265	2.016963	-0.171910
MO	2.237303	-1.173634	-0.218946
MO	-1.292371	-0.824062	-0.573250
O	1.209822	3.245161	-1.307038
O	0.792604	2.758154	1.354948
O	2.334179	0.711665	-0.245906
O	-0.615974	1.090447	-0.628857
O	2.448983	-1.764672	1.370571
O	3.400218	-1.889127	-1.221635
O	-1.962873	-1.081388	-2.101951
O	0.490637	-1.537390	-0.785060
O	-2.082685	-1.934868	0.445614
O	-2.970856	0.524332	0.074628
H	-2.829862	1.409155	-0.302683
C	-4.395444	0.178534	0.131467
H	-4.410501	-0.830310	0.544180
H	-4.856807	0.862496	0.850206
C	-5.060765	0.247782	-1.234743
H	-6.110981	-0.045321	-1.136408
H	-5.034577	1.264352	-1.642037
H	-4.576133	-0.429114	-1.941840
C	-0.733354	0.327705	2.916707
C	-1.334546	-0.716445	3.849059
H	-1.505664	0.968519	2.487721
H	-0.011571	0.967817	3.433260
H	-1.857568	-0.218984	4.672764
H	-2.042217	-1.355604	3.314843
H	-0.555179	-1.350147	4.286890
O	-0.068370	-0.285854	1.774886
H	0.539977	-0.969259	2.109026

TS (d1) ZPE=0.19097 E_{B,0K}=-1191.770034 E_{m,0K}=-1191.089455 E_{C,0K}=-1188.07575

MO	0.496532	2.078021	-0.088422
MO	2.426446	-0.792605	0.032062
MO	-1.002114	-1.058095	-0.884693
O	0.700348	3.417843	-1.103082
O	-0.016480	2.658652	1.423714
O	2.127369	1.070660	0.034244
O	-0.709353	0.875915	-0.849683
O	2.570427	-1.401689	1.617689
O	3.823282	-1.209770	-0.826202
O	-1.338834	-1.260852	-2.516041
O	0.861758	-1.496017	-0.757911
O	-1.896456	-2.420504	-0.102500
O	-2.875217	-0.426625	-0.083571
H	-2.784866	-1.702085	0.097205

C	-3.848037	0.410997	-0.736425
H	-3.342545	1.327705	-1.057075
H	-4.222167	-0.102612	-1.631622
C	-4.989573	0.731228	0.222483
H	-5.729463	1.361860	-0.281846
H	-5.489476	-0.183421	0.555557
H	-4.621823	1.268423	1.101594
C	-1.195861	-0.077846	2.677833
C	-1.665772	-1.222018	3.565142
H	-2.031193	0.396780	2.164313
H	-0.652723	0.682212	3.246692
H	-2.335336	-0.833562	4.339503
H	-2.204677	-1.975250	2.984449
H	-0.822701	-1.706836	4.070924
O	-0.318599	-0.554574	1.607435
H	0.330165	-1.159196	2.007579

Mo₃O₈(OC₂H₅)(OH)·C₂H₅OH (**e1**)

ZPE=0.193412 E_{B,0K}=-1191.811819 E_{m,0K}=-1191.12895 E_{C,0K}=-1188.11326

MO	0.712347	2.096111	0.083549
MO	2.288165	-0.876399	-0.218748
MO	-1.301653	-0.878101	-0.832136
O	0.764368	3.558744	-0.777905
O	0.477570	2.432804	1.737969
O	2.272377	1.028207	-0.181592
O	-0.615686	0.960085	-0.533919
O	2.177561	-1.483652	1.391715
O	3.638276	-1.531986	-1.012300
O	-1.757235	-0.772075	-2.436516
O	0.699005	-1.258224	-1.039220
O	-1.496600	-2.734465	-0.563732
O	-2.892670	-0.359412	-0.029772
H	-1.218097	-3.087155	0.297207
C	-4.091688	0.297953	-0.481278
H	-4.138097	0.214181	-1.573433
H	-4.926875	-0.262766	-0.047151
C	-4.118130	1.756078	-0.033536
H	-5.056863	2.212702	-0.364228
H	-4.060831	1.832896	1.055614
H	-3.288090	2.314667	-0.471969
C	-1.245978	-0.582221	2.738079
C	-1.136890	-1.507720	3.942173
H	-2.285858	-0.400013	2.465477
H	-0.759392	0.379944	2.925692
H	-1.607108	-1.035125	4.810849

H	-1.639735	-2.460987	3.753781
H	-0.090855	-1.707521	4.196464
O	-0.645448	-1.186375	1.552008
H	0.303715	-1.362237	1.733310

TS (**f1**) ZPE=0.18989 E_{B,0K}=-1191.776118 E_{C,0K}=-1188.087851

Mo	0.81824700	2.11967000	0.12304600
Mo	1.96669500	-1.07774500	-0.24190000
Mo	-1.29646300	-0.50041400	-0.84891900
O	1.48356800	3.35168800	-0.82862600
O	0.30069300	2.80985900	1.58383000
O	2.04533000	0.73129100	0.43639700
O	-0.62593300	1.27554900	-0.79243800
O	2.37372500	-2.30781800	0.84938200
O	3.19075300	-1.11206100	-1.40708000
O	-2.16786700	-0.65712700	-2.27350400
O	0.39059700	-1.25781300	-1.32833800
O	-1.47025300	-2.51867000	-0.08097300
O	-2.73922500	-0.17634300	0.30321500
H	-2.34084000	-2.72705000	0.28283800
C	-4.16445200	-0.15634000	0.13528500
H	-4.39660300	-0.28529100	-0.93221800
H	-4.57373000	-1.01059500	0.69662700
O	-0.14608100	-0.99682400	1.11679600
H	-0.80449300	-2.04354400	0.74196600
C	-0.32563300	-0.59428600	2.48721900
H	0.38084900	0.22005400	2.69743800
H	-1.34182400	-0.18928700	2.60767400
C	-4.72369600	1.15212800	0.67387500
H	-4.47602600	1.27564500	1.73552800
H	-4.32443500	2.00703800	0.11402800
H	-5.81745300	1.14581100	0.56809000
C	-0.08806200	-1.75629700	3.44230600
H	0.92318800	-2.16326600	3.32052800
H	-0.20486800	-1.41095300	4.47930000
H	-0.81128200	-2.56710100	3.27325800

Mo₃O₈(OC₂H₅)₂ · H₂O (**g1**) ZPE=0.192275 E_{B,0K}=-1191.79396 E_{C,0K}=-1188.101583

Mo	1.00921700	2.08002900	0.31529700
Mo	2.21944300	-1.03618500	-0.33385500
Mo	-1.38970800	-0.50412200	-0.47147100
O	0.99289400	3.20714800	-0.95172000
O	1.14719600	2.92854200	1.77699900
O	2.40689800	0.82946400	0.09925200
O	-0.56342600	1.03379500	0.31592600

O	2.43126300	-1.99398200	1.05793700
O	3.30956500	-1.55604500	-1.52787700
O	-1.78390900	-0.12563800	-2.08082400
O	0.47596400	-1.11116200	-0.91795000
O	-1.96981400	-2.56637700	-1.40090300
O	-3.06375300	0.08169300	0.15983400
H	-2.61476200	-2.57200200	-2.11954900
C	-4.03099900	0.95462000	-0.42307600
H	-3.91367000	0.91882800	-1.51804000
H	-5.01806100	0.55459300	-0.14756400
O	-1.49269600	-1.88838600	0.89114200
H	-2.26005800	-3.15009800	-0.68468900
C	-1.53850700	-1.62463400	2.30045600
H	-2.60004100	-1.57964800	2.59316200
H	-1.09243900	-0.64303900	2.52626700
C	-3.86793100	2.37817500	0.09682500
H	-3.95446300	2.40868200	1.19013800
H	-2.89628400	2.79419400	-0.19530700
H	-4.65819100	3.00830400	-0.33418500
C	-0.80729600	-2.72763900	3.05211500
H	0.25064300	-2.75954200	2.76211800
H	-0.87041900	-2.53870300	4.13332400
H	-1.26126100	-3.70546200	2.84310000

Mo₃O₈(OC₂H₅)₂ (**h**) (**B**)

ZPE=0.167403 E_{B,0K}=-1115.352924 E_{m,0K}=-1114.693633 E_{C,0K}=-1111.809522

MO	1.678655	1.725630	0.118746
MO	1.663254	-1.701709	0.064193
MO	-1.543035	-0.000463	-0.581344
O	2.387172	2.765231	-1.019330
O	1.750085	2.462962	1.648622
O	2.499174	0.006092	0.127545
O	-0.082708	1.313702	-0.318035
O	1.597644	-2.414908	1.605536
O	2.448739	-2.770642	-0.992895
O	-1.929686	-0.059254	-2.212548
O	-0.053548	-1.285644	-0.530524
O	-2.621458	1.341763	0.096924
C	-2.612984	2.422078	1.029812
H	-2.954397	2.025337	1.997837
H	-1.568833	2.752960	1.139581
C	-3.509744	3.546961	0.540909
H	-3.155502	3.937467	-0.421420
H	-4.544724	3.201301	0.424841
H	-3.495381	4.364382	1.275120

C	-3.323216	-3.323273	1.387034
C	-2.611440	-2.774879	0.162717
H	-4.340950	-2.919905	1.463931
H	-3.388310	-4.417302	1.305933
H	-2.771214	-3.076566	2.303013
H	-1.585069	-3.162989	0.086770
H	-3.147724	-3.023244	-0.765160
O	-2.527452	-1.345802	0.244667

Pathway 2

Mo₃O₉•C₂H₅OH•C₂H₅OH (c2) ZPE=0.194539 E_{B,0K}=-1191.796466 E_{C,0K}=-1188.094081

MO	-2.500660	1.088937	0.034772
MO	-1.289353	-2.177908	-0.031379
MO	1.131790	0.554864	0.007155
O	-3.171978	1.703400	1.467405
O	-3.292190	1.822758	-1.275721
O	-2.612636	-0.809050	-0.032721
O	-0.658229	1.410097	-0.038387
O	-1.379898	-3.128129	-1.431808
O	-1.444002	-3.198752	1.312736
O	2.151336	0.567206	1.360897
O	0.283941	-1.155342	0.036382
O	2.072420	0.586405	-1.409826
O	1.447730	2.812355	0.083603
H	0.728117	3.270888	-0.379827
C	2.737357	3.439288	-0.203027
H	3.028112	3.181618	-1.226283
H	3.430891	2.963320	0.491496
C	2.664297	4.942249	0.015308
H	2.369849	5.175781	1.041838
H	3.648219	5.383231	-0.172218
H	1.954554	5.414410	-0.673370
C	4.395068	-2.069369	0.573310
C	5.658411	-2.672885	-0.041182
H	4.032319	-2.698273	1.391086
H	4.604085	-1.074058	0.990225
H	5.453396	-3.670411	-0.440898
H	6.038891	-2.046819	-0.857275
H	6.449037	-2.754187	0.713273
O	3.303272	-1.997038	-0.356751
H	3.578988	-1.459983	-1.113991

TS (d2) ZPE=0.190993 E_{B,0K}=-1191.758597 E_{C,0K}=-1188.059261

MO	-2.367170	0.783410	0.214101
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MO	-0.901882	-2.318522	-0.219162
MO	1.299791	0.629688	-0.060194
O	-2.922878	1.232820	1.753301
O	-3.326195	1.559316	-0.951414
O	-2.353676	-1.108080	-0.009566
O	-0.556569	1.190179	-0.010064
O	-1.055302	-3.275947	-1.611060
O	-0.734431	-3.344730	1.123486
O	1.881074	0.762078	1.516158
O	0.541491	-1.132819	-0.342177
O	2.313188	1.155932	-1.501281
O	1.511226	2.783704	-0.229063
H	2.063532	2.256352	-1.255531
C	0.545017	3.824253	-0.069547
H	0.139890	3.767595	0.946938
H	-0.283135	3.683436	-0.776123
C	1.216851	5.177410	-0.299092
H	1.618012	5.246903	-1.314938
H	0.484331	5.980214	-0.162812
H	2.035851	5.326555	0.409927
C	3.765217	-1.500430	0.894299
C	4.925545	-2.366934	0.425288
H	2.974852	-2.104134	1.343386
H	4.083306	-0.746642	1.621573
H	4.589267	-3.113830	-0.298733
H	5.716163	-1.762277	-0.033047
H	5.361592	-2.886629	1.284290
O	3.130666	-0.832996	-0.234089
H	3.780810	-0.341169	-0.763753

Mo₃O₈(OC₂H₅)(OH)·C₂H₅OH (**e2**) ZPE=0.193615 E_{B,0K}=-1191.793988 E_{C,0K}=-1188.0945

MO	2.120181	-1.431397	-0.046727
MO	1.447259	1.943552	-0.213413
MO	-1.134086	-0.285948	0.682912
O	3.264803	-2.192349	0.942523
O	2.035454	-2.294143	-1.504640
O	2.559164	0.384485	-0.343165
O	0.430298	-1.370933	0.803613
O	0.824419	2.403627	-1.739708
O	2.244748	3.268975	0.485688
O	-1.674907	-0.046313	2.275081
O	0.060009	1.351851	0.833157
O	-1.104834	0.145871	-1.229602
O	-2.211023	-1.733639	0.223921
H	-0.876783	1.005756	-1.614881
C	-2.262194	-2.556609	-0.945497

H	-1.401512	-3.241498	-0.883557
H	-2.113735	-1.909861	-1.822569
C	-3.574618	-3.319567	-0.997562
H	-4.427029	-2.631638	-1.072952
H	-3.579056	-3.970562	-1.882757
H	-3.703206	-3.944375	-0.104779
C	-4.780580	2.417726	-0.526942
C	-3.999176	1.116296	-0.526278
H	-4.124850	3.269367	-0.747539
H	-5.564003	2.371956	-1.296071
H	-5.272695	2.592210	0.440852
H	-4.643848	0.252223	-0.309947
H	-3.490034	0.942144	-1.477927
O	-2.930223	1.151570	0.458370
H	-3.288000	1.264527	1.351449

TS (f2) ZPE=0.18957 E_{B,0K}=-1191.785738 E_{C,0K}=-1188.081271

MO	2.308075	1.208456	-0.241291
MO	1.230127	-1.944096	0.372871
MO	-1.278471	0.454871	-0.456457
O	2.981136	1.683200	-1.722176
O	2.970312	2.179971	0.980354
O	2.598046	-0.643235	0.084757
O	0.434097	1.335068	-0.251824
O	0.808253	-2.016874	2.029315
O	1.647554	-3.495550	-0.172947
O	-1.675298	0.464542	-2.090332
O	-0.216333	-1.255358	-0.538953
O	-1.586947	-0.161626	1.616075
O	-2.135483	1.993161	0.090168
H	-0.923784	-0.733393	2.035849
C	-2.149234	2.792687	1.277674
H	-2.339335	2.120490	2.125501
H	-1.132669	3.203156	1.388744
C	-3.189836	3.891561	1.153490
H	-2.978487	4.539380	0.293446
H	-4.195391	3.467128	1.040089
H	-3.173099	4.505265	2.064820
C	-4.661105	-2.476427	-0.321423
C	-3.324749	-1.970431	-0.838017
H	-5.440697	-1.712735	-0.437537
H	-4.957104	-3.367107	-0.892926
H	-4.596126	-2.757011	0.738594
H	-2.537849	-2.731485	-0.731600
H	-3.384055	-1.681482	-1.894509
O	-2.926256	-0.792621	-0.108414

H	-2.493173	-0.809672	0.955848
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Mo₃O₈(OC₂H₅)₂·H₂O (**g2**) ZPE=0.19322 E_{B,0K}=-1191.819519 E_{C,0K}=-1188.121997

MO	1.715524	1.686574	0.002642
MO	1.715520	-1.686587	0.002652
MO	-1.433830	-0.000002	-0.453369
O	2.537950	2.941633	-0.791252
O	1.478979	2.092406	1.655644
O	2.597268	-0.000008	-0.139891
O	0.075023	1.338795	-0.741702
O	1.478994	-2.092418	1.655655
O	2.537937	-2.941648	-0.791248
O	-2.014177	-0.000007	-2.024118
O	0.075013	-1.338809	-0.741681
O	-0.519443	0.000006	1.812142
O	-2.385121	1.409745	0.278684
H	-0.012398	0.778850	2.108470
C	-2.776313	2.707379	-0.187355
H	-3.255077	2.583435	-1.170975
H	-1.854963	3.293779	-0.321917
C	-3.707568	3.360122	0.819363
H	-3.212855	3.472882	1.792275
H	-3.990670	4.357082	0.454191
H	-4.620715	2.766135	0.951801
C	-3.707687	-3.360046	0.819331
C	-2.776335	-2.707359	-0.187333
H	-4.620833	-2.766036	0.951676
H	-3.990780	-4.357012	0.454169
H	-3.213056	-3.472786	1.792288
H	-1.854986	-3.293781	-0.321802
H	-3.255014	-2.583429	-1.170996
O	-2.385151	-1.409721	0.278696
H	-0.012405	-0.778834	2.108491

For M=W (Figure S4)

W₃O₉ (**a**) ZPE=0.030915 E_{B,0K}=-880.2015246 E_{m,0K}=-879.754381 E_{C,0K}=-877.1685669

W	0.000000	1.769351	-1.021526
W	0.000000	-1.769351	-1.021526
W	0.000000	0.000000	2.043079
O	-1.382087	2.635048	-1.521337
O	1.382087	2.635048	-1.521337
O	0.000000	0.000000	-1.728172
O	0.000000	1.496649	0.864099
O	1.382087	-2.635048	-1.521337

O	-1.382087	-2.635048	-1.521337
O	-1.382210	0.000000	3.042530
O	0.000000	-1.496649	0.864099
O	1.382210	0.000000	3.042530

W₃O₉·C₂H₅OH (b)

ZPE=0.112711 E_{B,0K}=-1035.297708 E_{m,0K}=-1034.747534 E_{C,0K}=-1031.877291

W	0.618812	2.021697	-0.001392
W	2.102859	-1.111882	0.006347
W	-1.541421	-0.950041	-0.022513
O	0.644525	2.986600	-1.415263
O	0.633361	3.055447	1.363740
O	2.075810	0.792739	0.027641
O	-0.912162	0.940122	0.025093
O	2.819588	-1.733328	1.429166
O	2.965137	-1.710847	-1.343313
O	-2.246647	-1.744074	-1.364785
O	0.278992	-1.562591	-0.094510
O	-2.130414	-1.673388	1.412466
O	-3.355798	0.309013	-0.060649
H	-3.242948	1.149924	0.406258
C	-4.690374	-0.260146	0.177146
H	-4.753201	-1.087203	-0.536019
H	-4.703812	-0.663405	1.197322
C	-5.758144	0.787855	-0.056493
H	-6.744371	0.332583	0.106814
H	-5.662124	1.627676	0.647517
H	-5.720081	1.173294	-1.083116

Pathway 1

W₃O₉·C₂H₅OH·C₂H₅OH (c1)

ZPE=0.196325 E_{B,0K}=-1190.379948 E_{m,0K}=-1189.732598 E_{C,0K}=-1186.580818

W	0.598568	1.941084	-0.437081
W	2.176187	-1.068164	0.068394
W	-1.408043	-1.076159	-0.291527
O	0.753960	2.859516	-1.873517
O	0.429541	3.056423	0.858761
O	2.127851	0.791191	-0.287681
O	-0.893099	0.827905	-0.627897
O	2.500218	-1.344552	1.740942
O	3.357274	-1.875202	-0.871835
O	-2.008540	-1.834582	-1.701263

O	0.442671	-1.641173	-0.333307
O	-2.066430	-1.923849	1.047750
O	-3.277365	0.113985	-0.178860
H	-3.215794	0.902455	-0.743949
C	-4.599750	-0.520456	-0.300993
H	-4.637069	-1.032267	-1.266671
H	-4.613365	-1.263388	0.496359
C	-5.700351	0.514842	-0.146068
H	-6.671560	0.015129	-0.212489
H	-5.637185	1.018882	0.821866
H	-5.662175	1.266531	-0.942407
C	-0.452969	0.956898	3.173727
C	-1.886938	1.392972	2.920402
H	0.195436	1.827206	3.315315
H	-0.398883	0.319887	4.062886
H	-2.248176	1.959104	3.785035
H	-1.944276	2.044809	2.045116
H	-2.537529	0.526817	2.773596
O	0.047225	0.190832	2.035820
H	0.767511	-0.374936	2.367422

TS (d1) ZPE=0.19097 E_{B,0K}=-1190.348088 E_{m,0K}=-1189.69992 E_{C,0K}=-1186.545692

W	0.427023	2.050973	-0.128511
W	2.213825	-0.905016	0.062677
W	-1.264683	-1.052539	-0.657061
O	0.639884	3.313244	-1.264465
O	0.025691	2.762534	1.381664
O	2.013770	0.975785	-0.016841
O	-0.897237	0.875560	-0.723484
O	2.368621	-1.438849	1.693244
O	3.568466	-1.447670	-0.828814
O	-1.682800	-1.317127	-2.279594
O	0.592921	-1.570140	-0.629538
O	-2.133246	-2.372215	0.230044
O	-3.091113	-0.354527	0.145500
H	-3.027296	-1.593827	0.388523
C	-4.091065	0.435064	-0.539330
H	-3.605982	1.351896	-0.887883
H	-4.440919	-0.122147	-1.416807
C	-5.243595	0.752248	0.404636
H	-5.996246	1.348646	-0.121543
H	-5.722538	-0.164815	0.760965
H	-4.894952	1.323933	1.269554
C	-1.244799	0.131301	2.787129
C	-1.725031	-0.935831	3.758939
H	-2.077227	0.619062	2.281627

H	-0.635860	0.893433	3.279873
H	-2.338096	-0.468880	4.536641
H	-2.325643	-1.693622	3.249520
H	-0.882897	-1.430872	4.255595
O	-0.438237	-0.452878	1.706833
H	0.204578	-1.062110	2.113584

W₃O₈(OC₂H₅)(OH)·C₂H₅OH (e1)

ZPE=0.193078 E_{B,0K}=-1190.397418 E_{m,0K}=-1189.748151 E_{C,0K}=-1186.592308

W	0.723162	2.033724	-0.056450
W	2.051665	-1.068739	-0.100031
W	-1.545201	-0.866204	-0.596095
O	0.831885	3.384051	-1.110820
O	0.597484	2.583306	1.569982
O	2.196583	0.826640	-0.249402
O	-0.720393	0.942225	-0.455478
O	1.918058	-1.505399	1.579343
O	3.333152	-1.926646	-0.852293
O	-2.023535	-0.837037	-2.216537
O	0.409418	-1.417511	-0.837053
O	-1.899013	-2.682108	-0.219856
O	-3.076605	-0.175728	0.191163
H	-1.695609	-3.042887	0.655440
C	-4.287794	0.459941	-0.267731
H	-4.343022	0.339490	-1.355304
H	-5.115757	-0.089842	0.192020
C	-4.314290	1.930838	0.131921
H	-5.255105	2.376485	-0.207663
H	-4.251085	2.044654	1.217636
H	-3.488137	2.477357	-0.329275
C	-1.316191	-0.219540	2.864297
C	-1.128979	-0.958902	4.180818
H	-2.368053	-0.025017	2.654836
H	-0.773894	0.730563	2.856140
H	-1.493005	-0.334190	5.002992
H	-1.685953	-1.900402	4.189264
H	-0.072127	-1.173979	4.368544
O	-0.849555	-1.031284	1.737720
H	0.093137	-1.270090	1.896017

TS (f1) ZPE=0.18889 E_{B,0K}=-1190.350654 E_{C,0K}=-1186.562061

W	0.54424800	2.09531200	0.03144600
W	1.90678100	-1.03782700	-0.15969600

W	-1.43802400	-0.72059800	-0.62138200
O	1.06650100	3.32905500	-1.03020600
O	0.03439200	2.82359700	1.49620700
O	1.89974300	0.82503900	0.35506400
O	-0.87198600	1.09740700	-0.75441900
O	2.39696000	-2.15392200	1.04383100
O	3.10322200	-1.12393800	-1.37295000
O	-2.33423200	-1.01916600	-2.02791200
O	0.29555700	-1.40334900	-1.12233000
O	-1.44707300	-2.64970700	0.30787000
O	-2.86001300	-0.35343200	0.53562100
H	-2.28237200	-2.90781800	0.72013800
C	-4.28845100	-0.21862500	0.40358400
H	-4.57837800	-0.57886800	-0.59402300
H	-4.74281400	-0.86413400	1.16851900
O	-0.19648100	-0.93180500	1.29871200
H	-0.77958100	-2.08344200	1.06146400
C	-0.34205700	-0.44097100	2.65044400
H	0.33407500	0.41443900	2.77420400
H	-1.36964600	-0.07179800	2.78210800
C	-0.01389300	-1.52831900	3.66291200
H	-0.09371000	-1.12076400	4.68039000
H	-0.71331300	-2.37336000	3.58332000
H	1.00509700	-1.90526200	3.51319700
C	-4.69258400	1.23192700	0.61060500
H	-4.37371600	1.59092000	1.59715100
H	-4.25233200	1.87565600	-0.16130100
H	-5.78654400	1.31249100	0.54648000

W₃O₈(OC₂H₅)₂·H₂O (**g1**) ZPE=0.193313 E_{B,0K}=-1190.374815 E_{C,0K}=-1186.566523

W	1.103821	1.983866	0.278517
W	1.921155	-1.336058	-0.253645
W	-1.559946	-0.306389	-0.381275
O	1.586196	3.290640	-0.714537
O	1.045127	2.533307	1.898254
O	2.287092	0.517932	0.110198
O	-0.585314	1.324468	-0.263305
O	2.060270	-2.291578	1.170238
O	2.951343	-1.987703	-1.461204
O	-2.011485	-0.384889	-2.042324
O	0.174068	-1.320918	-0.831456
O	-2.425612	-2.439160	-0.581910
O	-3.208127	0.372015	0.160906
H	-2.466305	-2.562672	-1.544203
C	-4.352987	0.844225	-0.563243
H	-4.245950	0.532340	-1.612691

H	-5.229135	0.351162	-0.119469
O	-1.277020	-0.975240	1.381905
H	-1.843218	-3.129205	-0.232816
C	-1.229238	-2.008674	2.350413
H	-0.848246	-2.931512	1.880822
H	-0.483631	-1.713404	3.102079
C	-2.590255	-2.234156	2.996207
H	-2.943473	-1.314243	3.478951
H	-3.337100	-2.546169	2.253973
H	-2.508982	-3.019829	3.760223
C	-4.459868	2.356983	-0.442063
H	-4.535299	2.662410	0.609083
H	-3.588079	2.847430	-0.893559
H	-5.361077	2.697376	-0.970558

W₃O₈(OC₂H₅)₂ (h) (B)

ZPE=0.167117 E_{B,0K}=-1113.932037 E_{m,0K}=-1113.308838 E_{C,0K}=-1110.279282

W	-1.543639	-1.718796	0.095784
W	-1.542697	1.719542	0.096202
W	1.714933	-0.000478	-0.444686
O	-2.139725	-2.646081	-1.215355
O	-1.771264	-2.602499	1.547546
O	-2.363438	0.000587	0.180045
O	0.262040	-1.310355	-0.136216
O	-1.769743	2.602995	1.548209
O	-2.138309	2.647521	-1.214667
O	1.870303	-0.000063	-2.131692
O	0.262710	1.310035	-0.136006
O	2.833152	-1.340443	0.164791
C	3.015293	-2.761549	0.212469
H	3.473253	-3.062947	-0.740277
H	2.015608	-3.214105	0.282835
C	3.885691	-3.140228	1.397020
H	3.413716	-2.841008	2.341700
H	4.024517	-4.230105	1.409116
H	4.872476	-2.665215	1.325944
C	3.888338	3.139293	1.394804
C	3.016776	2.759762	0.211386
H	4.874837	2.663732	1.323413
H	4.027698	4.229115	1.405629
H	3.417003	2.841289	2.340187
H	2.017394	3.212935	0.282077
H	3.474096	3.059886	-0.742076
O	2.833853	1.338666	0.165492

Pathway 2

W₃O₉·C₂H₅OH·C₂H₅OH (c2) ZPE=0.195847 E_{B,0K}=-1190.365498 E_{C,0K}=-1186.557636

W	-1.623967	1.700027	0.158880
W	-1.604014	-1.735324	-0.155468
W	1.653125	0.009404	-0.014603
O	-2.003879	2.447787	1.656692
O	-2.099670	2.746803	-1.115585
O	-2.428150	-0.020923	0.009936
O	0.204260	1.335488	0.056483
O	-2.018266	-2.490917	-1.639064
O	-2.030440	-2.780501	1.137841
O	2.504147	-0.125041	1.481958
O	0.208906	-1.307053	-0.091220
O	2.577142	0.147576	-1.468212
O	2.718492	2.100638	0.244594
H	2.656146	2.391790	1.168556
C	2.551304	3.228960	-0.660960
H	1.528416	3.609573	-0.577297
H	2.687106	2.800299	-1.654490
C	3.580915	4.312392	-0.373115
H	4.596846	3.918891	-0.463105
H	3.458886	5.130056	-1.090569
H	3.453430	4.731652	0.631360
C	2.921797	-3.016612	0.806276
C	3.576012	-4.298648	0.311320
H	1.946615	-3.213938	1.253995
H	3.540310	-2.491118	1.539588
H	2.941302	-4.807485	-0.419062
H	4.550613	-4.098869	-0.148487
H	3.741520	-4.973002	1.157472
O	2.643003	-2.115812	-0.305804
H	3.453640	-1.942667	-0.811869

TS (d2) ZPE=0.19091 E_{B,0K}=-1190.334231 E_{C,0K}=-1186.52253

W	-1.830171	1.477980	0.173155
W	-1.356900	-1.917288	-0.172109
W	1.640450	0.240722	-0.053867
O	-2.238399	2.139779	1.701511
O	-2.498354	2.468491	-1.057616
O	-2.400781	-0.334550	0.015788
O	0.024076	1.328046	-0.025182
O	-1.776127	-2.804967	-1.578142
O	-1.502587	-2.941231	1.197360

O	2.225487	0.227839	1.548049
O	0.377263	-1.225384	-0.294605
O	2.761702	0.398089	-1.509824
O	2.466075	2.207519	-0.275479
H	2.843510	1.562404	-1.271658
C	1.902589	3.514639	-0.097995
H	1.520787	3.581792	0.925969
H	1.061418	3.653524	-0.788176
C	2.976990	4.570665	-0.340067
H	3.361730	4.510443	-1.362842
H	2.552016	5.569006	-0.192012
H	3.811179	4.439620	0.354630
C	3.286098	-2.506811	0.967281
C	4.117480	-3.697982	0.516068
H	2.339259	-2.822660	1.407486
H	3.815778	-1.879988	1.690447
H	3.570084	-4.308932	-0.206474
H	5.063237	-3.378243	0.064454
H	4.358868	-4.319591	1.383832
O	2.908450	-1.682164	-0.177627
H	3.678728	-1.446783	-0.722503

W₃O₈(OC₂H₅)(OH)·C₂H₅OH (e2) ZPE=0.193732 E_{B,0K}=-1190.377123 E_{C,0K}=-1186.569715

W	-1.922237	-1.439630	0.044112
W	-1.212955	1.924818	0.165482
W	1.404818	-0.340175	-0.563422
O	-3.007483	-2.198763	-1.038157
O	-1.964036	-2.287913	1.531001
O	-2.360226	0.394165	0.287225
O	-0.174356	-1.426651	-0.663479
O	-0.628735	2.396974	1.721084
O	-1.950556	3.266998	-0.603715
O	1.955982	-0.212640	-2.185626
O	0.215859	1.288143	-0.806506
O	1.312943	0.161861	1.334674
O	2.451268	-1.779166	-0.021138
H	1.001672	0.994318	1.723035
C	2.504652	-2.577309	1.171140
H	1.646042	-3.264187	1.126520
H	2.361982	-1.910356	2.032703
C	3.817695	-3.336769	1.233758
H	4.669900	-2.646560	1.290074
H	3.828144	-3.969601	2.131971
H	3.942601	-3.979326	0.353057
C	4.811822	2.579869	0.561257
C	4.144139	1.221492	0.656593

H	4.075367	3.387474	0.655976
H	5.545157	2.679630	1.373322
H	5.349547	2.699800	-0.390333
H	4.865912	0.398055	0.565188
H	3.582776	1.097407	1.585389
O	3.145250	1.063689	-0.395622
H	3.541485	1.125141	-1.278009

TS (f2) ZPE=0.189689 E_{B,0K}=-1190.367814 E_{C,0K}=-1186.56563

W	-1.497733	-1.732944	0.220365
W	-1.475559	1.666799	-0.056173
W	1.459063	-0.193747	-0.571320
O	-2.551293	-2.826844	-0.561414
O	-1.101910	-2.381885	1.759919
O	-2.298712	-0.020016	0.352105
O	0.061274	-1.489685	-0.834860
O	-1.231186	2.701692	1.290205
O	-2.464401	2.504767	-1.170585
O	2.314313	-0.021303	-2.026761
O	0.137610	1.244255	-0.911804
O	0.549435	0.143406	1.457166
O	2.578522	-1.425064	0.246325
H	0.578127	-0.508604	2.170164
C	3.843120	-2.056865	0.000207
H	4.184064	-1.755150	-1.001146
H	3.651271	-3.139044	0.001541
C	4.844562	-1.678539	1.078658
H	4.483106	-1.979876	2.069915
H	5.795610	-2.193058	0.883760
H	5.028815	-0.596874	1.080586
C	2.986868	3.428429	1.519568
C	2.597602	2.668503	0.265502
H	3.889073	3.003301	1.977989
H	3.191736	4.475087	1.255860
H	2.169970	3.418316	2.253219
H	1.689410	3.082293	-0.189631
H	3.400282	2.674028	-0.482034
O	2.359471	1.271636	0.595234
H	1.533589	0.974763	1.359380

W₃O₈(OC₂H₅)₂ · H₂O (g2) ZPE=0.193471 E_{B,0K}=-1190.404733 E_{C,0K}=-1186.599136

W	1.553961	1.686148	0.014651
W	1.554407	-1.686049	0.014111
W	-1.610776	-0.000257	-0.374806
O	2.359621	2.962668	-0.796885

O	1.335681	2.078508	1.688653
O	2.442507	0.000212	-0.144382
O	-0.107791	1.340656	-0.691611
O	1.336289	-2.078884	1.688023
O	2.360382	-2.962123	-0.797819
O	-2.223540	-0.000751	-1.950713
O	-0.107439	-1.340782	-0.691971
O	-0.644484	-0.000526	1.834907
O	-2.566762	1.399772	0.373612
H	-0.138995	0.781387	2.133195
C	-3.074761	2.662408	-0.085948
H	-3.517800	2.505358	-1.080702
H	-2.213810	3.338567	-0.190802
C	-4.086692	3.204463	0.907113
H	-3.627774	3.344397	1.894113
H	-4.455962	4.176930	0.552972
H	-4.941630	2.523614	1.006921
C	-4.087488	-3.203058	0.910382
C	-3.078120	-2.661154	-0.085389
H	-4.940853	-2.520853	1.014306
H	-4.459710	-4.174298	0.555970
H	-3.625330	-3.345387	1.895524
H	-2.218685	-3.338616	-0.194278
H	-3.524365	-2.501886	-1.078358
O	-2.566409	-1.400109	0.374274
H	-0.139005	-0.782608	2.132798



For M=Mo (Figure S5a)

Pathway 1

TS (b1) ZPE=0.161109 $E_{\text{B},0\text{K}}=-1115.290559$ $E_{\text{C},0\text{K}}=-1111.745860$

MO	1.704662	1.700908	0.051393
MO	1.784045	-1.730258	0.013153
MO	-1.571372	-0.107411	-0.167482
O	2.195780	2.636335	-1.280720
O	2.002310	2.582113	1.474501
O	2.567847	0.002660	0.078682
O	-0.087343	1.247856	-0.082796
O	2.097615	-2.622939	1.426059
O	2.332969	-2.623176	-1.324763
O	-2.313951	-1.045786	-1.461543
O	-0.021474	-1.338368	-0.134148
O	-2.606314	1.429439	-0.343427

C	-2.555666	2.840724	-0.517759
H	-1.500736	3.133423	-0.616647
H	-3.071264	3.065282	-1.463418
C	-3.219303	3.550393	0.652939
H	-4.267971	3.243122	0.756022
H	-2.691213	3.333695	1.590467
H	-3.190266	4.635616	0.482376
C	-3.771018	-2.857365	-0.255946
C	-3.535474	-2.525415	1.084380
H	-3.079165	-1.994642	-0.895126
H	-3.286806	-3.762876	-0.632978
H	-4.767696	-2.648304	-0.653590
H	-4.252991	-1.942725	1.657454
H	-2.755795	-3.021774	1.658089
O	-2.314367	-0.811496	1.230528

Mo₃O₈(OC₂H₅)(OH)·C₂H₄ (**c1**)

ZPE=0.163062

E_{B,0K}=-1115.326586

E_{C,0K}=-1111.780583

MO	-1.829522	1.668176	0.057982
MO	-1.878652	-1.765848	0.200349
MO	1.322664	-0.145153	-0.611531
O	-1.816079	2.478439	1.551367
O	-2.584788	2.661570	-1.090239
O	-2.669590	-0.033231	0.194668
O	-0.091738	1.217039	-0.451241
O	-2.702698	-2.851361	-0.807631
O	-1.830397	-2.415298	1.767091
O	2.221772	-1.278621	0.594457
O	-0.159382	-1.394126	-0.435117
O	2.477734	1.267994	-0.209945
C	2.574188	2.156999	0.902143
H	1.587824	2.628893	1.036672
H	2.788664	1.556263	1.801362
C	3.655161	3.195579	0.653263
H	4.636120	2.720287	0.524992
H	3.427948	3.784786	-0.244067
H	3.708383	3.876771	1.513660
C	5.308801	-2.176560	1.107438
C	5.462678	-1.435645	0.002584
H	3.197354	-1.355648	0.588677
H	5.026366	-3.229376	1.056189
H	5.479165	-1.763565	2.103131
H	5.763786	-0.388029	0.052683
H	5.312558	-1.854262	-0.994001
O	1.812450	-0.429869	-2.188100

Mo₃O₈(OC₂H₅)(OH) (**d**) (**A**)

ZPE=0.111406 E_{B,0K}=-1036.72078 E_{C,0K}=-1033.401804

MO	0.556327	2.022903	-0.197569
MO	2.112005	-1.006069	0.304808
MO	-1.453722	-1.032919	-0.508834
O	0.806158	3.124369	-1.460550
O	0.171935	2.891201	1.210985
O	2.054125	0.885500	0.071781
O	-0.814474	0.809521	-0.589082
O	2.319490	-1.415453	1.937224
O	3.354863	-1.726511	-0.592643
O	-1.805658	-1.592436	-2.048046
O	0.417210	-1.502980	-0.317522
O	-1.665024	-2.420971	0.793199
O	-3.125727	-0.393023	-0.004408
H	-2.553290	-2.773486	0.942906
C	-3.795799	0.047870	1.177206
H	-4.870236	-0.078005	0.984144
H	-3.503354	-0.619997	2.004155
C	-3.469337	1.499149	1.509620
H	-2.408504	1.633768	1.753564
H	-3.727135	2.156983	0.670702
H	-4.063451	1.800448	2.383086

Pathway 2

TS (b2) ZPE=0.160962 E_{B,0K}=-1115.272022 E_{C,0K}=-1111.732567

MO	0.155207	2.270402	0.345542
MO	2.349025	-0.239185	-0.391975
MO	-1.355068	-1.028614	-0.325744
O	-0.164379	3.741290	-0.442562
O	0.002756	2.498741	2.025351
O	1.878512	1.583597	-0.081826
O	-0.981183	0.923646	-0.235304
O	3.123464	-0.953054	0.967920
O	3.340649	-0.434004	-1.761960
O	-1.645997	-1.639516	-1.876163
O	0.739463	-1.055331	-0.612929
O	-3.094418	-0.572574	0.184768
C	-4.081383	0.219841	-0.479891
H	-4.213374	-0.181854	-1.497986
H	-3.689154	1.245492	-0.563399
C	-5.382946	0.192482	0.304152
H	-5.237088	0.596494	1.314272
H	-6.132532	0.808213	-0.212530
H	-5.769593	-0.831681	0.384821

C	1.290308	-3.350710	2.057867
C	0.742182	-3.836801	0.870516
H	0.302394	-2.675834	1.871251
H	1.116224	-3.896841	2.985685
H	2.125198	-2.645188	2.001875
H	1.000996	-3.383382	-0.087295
H	0.004564	-4.640076	0.866321
O	-1.096551	-2.324488	0.839278

Mo₃O₈(OC₂H₅)(OH)·C₂H₄ (**c2**)

ZPE=0.163011

E_{B,0K}=-1115.326612

E_{C,0K}=-1111.781516

MO	1.812482	1.679593	0.065828
MO	1.894963	-1.754718	0.206851
MO	-1.316980	-0.162760	-0.625476
O	2.569789	2.682953	-1.072419
O	1.774814	2.486638	1.560656
O	2.667445	-0.014142	0.208688
O	0.085276	1.212189	-0.462861
O	1.852616	-2.411839	1.770458
O	2.731842	-2.826640	-0.804976
O	-1.792016	-0.460546	-2.204228
O	0.172114	-1.398853	-0.429177
O	-2.486400	1.243026	-0.241043
C	-2.598555	2.141262	0.862231
H	-2.824978	1.547405	1.763129
H	-1.614339	2.614598	1.006618
C	-3.676603	3.176920	0.589899
H	-3.435541	3.761520	-0.306784
H	-4.654559	2.699450	0.448165
H	-3.744552	3.862973	1.445358
C	-5.401631	-1.761344	-0.048843
C	-5.362523	-1.834743	1.287479
H	-3.192777	-1.361891	0.586369
H	-5.180774	-2.626437	-0.675941
H	-5.673897	-0.839380	-0.564833
H	-5.605406	-0.975950	1.915315
H	-5.108459	-2.761997	1.803244
O	-2.216527	-1.295497	0.581432

For M=W (Figure S6b)

Pathway 1

TS	(b1)	ZPE=0.16109	E _{B,0K} =-1113.870823	E _{C,0K} =-1110.2176
W		1.584561	1.665057	0.007221
W		1.542349	-1.768090	0.053255

W	-1.756116	-0.036255	-0.204577
O	2.144081	2.616379	-1.307715
O	1.861599	2.513601	1.473847
O	2.400956	-0.062715	0.026517
O	-0.225558	1.281170	-0.180375
O	1.739566	-2.555536	1.566898
O	2.116888	-2.795501	-1.196400
O	-2.598564	-0.965263	-1.454771
O	-0.243203	-1.312446	-0.217161
O	-2.744406	1.530501	-0.373676
C	-2.707287	2.958284	-0.333895
H	-1.691880	3.283190	-0.600252
H	-3.402107	3.314690	-1.107239
C	-3.106302	3.484176	1.035579
H	-4.119982	3.156667	1.298530
H	-2.407307	3.132524	1.804839
H	-3.087325	4.583847	1.029383
C	-4.124244	-2.664684	-0.174729
C	-3.847145	-2.315605	1.153948
H	-3.402632	-1.866880	-0.843399
H	-3.713690	-3.614293	-0.530105
H	-5.111738	-2.398244	-0.561217
H	-4.503213	-1.654895	1.715558
H	-3.101121	-2.853341	1.734775
O	-2.474846	-0.693805	1.242478

W₃O₈(OC₂H₅)(OH)·C₂H₄ (c1)
1110.255894

ZPE=0.162802

E_{B,0K}=-1113.906575 E_{C,0K}=-

W	-1.697522	1.634485	0.007180
W	-1.598260	-1.795306	0.169404
W	1.598636	-0.032782	-0.431748
O	-1.911121	2.537221	1.449318
O	-2.345857	2.521644	-1.306305
O	-2.474098	-0.101109	0.141905
O	0.114623	1.262360	-0.250509
O	-2.283799	-2.891923	-0.952318
O	-1.656325	-2.491589	1.733543
O	2.580633	-1.226922	0.634213
O	0.157977	-1.344631	-0.292226
O	2.667760	1.410667	0.061952
C	2.731163	2.337450	1.151592
H	1.724299	2.762140	1.283160
H	2.990324	1.773906	2.061493
C	3.754770	3.419826	0.857842
H	4.755304	2.988940	0.724126
H	3.484657	3.974358	-0.049693

H	3.788807	4.124716	1.699900
C	5.570570	-2.406824	0.856393
C	5.789036	-1.374345	0.032177
H	3.548790	-1.359118	0.588899
H	5.252468	-3.380897	0.481603
H	5.721042	-2.321979	1.933730
H	6.127330	-0.406541	0.405580
H	5.658639	-1.464851	-1.047336
O	2.083201	-0.203302	-2.042988

W₃O₈(OC₂H₅)(OH) (d) (A)

ZPE=0.110809 E_{B,0K}=-1035.301639 E_{C,0K}=-1031.872335

W	0.510277	2.026465	-0.091054
W	2.060653	-1.035135	0.193826
W	-1.598250	-1.011007	-0.316322
O	0.654920	3.069757	-1.440010
O	0.284141	2.971378	1.320916
O	2.012561	0.866958	0.075559
O	-0.919157	0.835651	-0.298198
O	2.546883	-1.547125	1.753172
O	3.115372	-1.720562	-0.965489
O	-1.965597	-1.491180	-1.895573
O	0.273288	-1.498376	-0.140201
O	-1.876714	-2.476121	0.864077
O	-3.222146	-0.255729	0.183050
H	-2.753989	-2.849117	1.018599
C	-3.724061	0.573431	1.239433
H	-3.047993	1.437636	1.326686
H	-3.670186	-0.002577	2.176532
C	-5.146498	1.005664	0.932737
H	-5.810978	0.136604	0.844846
H	-5.514285	1.644358	1.747563
H	-5.185863	1.577376	-0.002947

Pathway 2

TS (b2) ZPE=0.160808 E_{B,0K}=-1113.851045 E_{C,0K}=-1110.200769

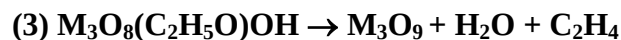
W	0.467517	2.195502	0.250916
W	2.129829	-0.752395	-0.258627
W	-1.626342	-0.844442	-0.286307
O	0.444207	3.556891	-0.792180
O	0.345407	2.729834	1.877958
O	2.036839	1.134501	0.007234
O	-0.911885	1.017760	-0.147966

O	2.618732	-1.593651	1.176155
O	3.164742	-1.195184	-1.555712
O	-2.063865	-1.378008	-1.847363
O	0.399648	-1.220158	-0.613173
O	-3.251293	-0.106079	0.262966
C	-4.187594	0.776054	-0.366765
H	-4.373879	0.401611	-1.385813
H	-3.716908	1.768096	-0.442750
C	-5.468026	0.839749	0.447891
H	-5.266075	1.208826	1.461795
H	-6.176244	1.525601	-0.037883
H	-5.935894	-0.150791	0.518377
C	0.424786	-3.672658	2.203031
C	-0.126701	-4.036768	0.974683
H	-0.406779	-2.820264	1.967241
H	0.090965	-4.183775	3.106634
H	1.378771	-3.137235	2.211291
H	0.277642	-3.645268	0.040967
H	-1.002351	-4.682888	0.906983
O	-1.604820	-2.198834	0.864260

W₃O₈(OC₂H₅)(OH)·C₂H₄ (c2) ZPE=0.163041 E_{B,0K}=-1113.909364 E_{C,0K}=-1110.256407

W	-0.817534	-2.153144	0.292822
W	-2.001246	1.029147	-0.205549
W	1.688408	0.497876	-0.338793
O	-1.024483	-3.491795	-0.754544
O	-0.759861	-2.718516	1.909626
O	-2.189421	-0.852234	0.072815
O	0.745658	-1.208431	-0.122141
O	-2.676006	1.949041	1.077391
O	-2.713655	1.527085	-1.681974
O	1.981444	0.691935	-1.994700
O	-0.157419	1.250845	-0.238255
O	3.217284	-0.373932	0.205087
C	4.199638	-1.322994	-0.234847
H	4.396389	-1.126074	-1.298947
H	3.741770	-2.318302	-0.137624
C	5.456377	-1.204692	0.607798
H	5.236506	-1.392908	1.666340
H	6.189104	-1.948703	0.266009
H	5.902232	-0.206926	0.508612
C	0.049129	4.511533	1.064273
C	1.166553	4.865378	1.712185
H	1.638609	2.836010	0.771559
H	-0.750709	3.953833	1.553832
H	-0.114967	4.788599	0.021539

H	1.953855	5.442591	1.224602
H	1.324002	4.610552	2.761487
O	2.189035	2.050867	0.574018



For M=Mo (Figure S6a)

TS (b) ZPE=0.105764 $E_{\text{B},0\text{K}}=-1036.664559$ $E_{\text{m},0\text{K}}=-1036.0762$ $E_{\text{C},0\text{K}}=-1033.345914$

MO	-1.806921	-1.563147	0.171216
MO	-1.327945	1.863715	0.091467
MO	1.617696	-0.353987	-0.530181
O	-2.654704	-2.423397	-1.020293
O	-2.029367	-2.350967	1.658826
O	-2.342736	0.256135	0.252834
O	0.012293	-1.396479	-0.242763
O	-1.317084	2.756029	1.539835
O	-1.908436	2.863288	-1.153708
O	2.066420	-0.911694	-2.057543
O	0.369867	1.215406	-0.289704
O	2.901549	1.227405	-0.535441
O	2.624982	-1.138113	0.666736
H	2.482806	2.073165	-0.306702
C	4.481836	-0.735031	1.443012
H	4.042752	-0.940978	2.412880
H	4.842573	-1.596826	0.891753
C	4.867361	0.570284	1.078345
H	3.925281	0.952188	0.312289
H	4.852527	1.318130	1.870879
H	5.697749	0.645456	0.375451

$\text{Mo}_3\text{O}_9 \cdot \text{C}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (c)

ZPE=0.109097 $E_{\text{B},0\text{K}}=-1036.709834$ $E_{\text{m},0\text{K}}=-1036.122914$ $E_{\text{C},0\text{K}}=-1033.399521$

MO	-2.086285	-1.433702	0.042066
MO	-1.218232	1.946897	0.011308
MO	1.450853	-0.568903	-0.092268
O	-2.841821	-2.179668	-1.278235
O	-2.654546	-2.171568	1.457758
O	-2.386073	0.442795	0.061889
O	-0.209835	-1.522435	-0.085395
O	-1.412156	2.951915	1.364921
O	-1.462705	2.884004	-1.381484
O	2.235668	-1.169010	-1.469896
O	0.475913	1.149658	0.007520

O	3.045936	1.058378	-0.203732
O	2.256364	-1.147039	1.284997
H	2.855425	1.838292	0.340302
C	5.604026	-0.758348	0.170362
H	5.271646	-1.278752	1.065128
H	5.417789	-1.250224	-0.781603
C	6.223429	0.431547	0.235880
H	3.968221	0.761705	-0.024251
H	6.430951	0.912033	1.189499
H	6.571202	0.941280	-0.659703

Mo₃O₉·H₂O (**d**) ZPE=0.055917 E_{B,0K}=-958.1030075 E_{C,0K}=-955.0163515

MO	-0.529917	1.999408	0.000004
MO	-1.787726	-1.249890	0.000031
MO	1.786138	-0.780426	-0.000012
O	-0.647535	2.986906	1.370685
O	-0.647655	2.986868	-1.370692
O	-1.872414	0.646930	0.000080
O	1.075643	1.023078	-0.000044
O	-2.540915	-1.901492	-1.367926
O	-2.540879	-1.901561	1.367975
O	2.550696	-1.382237	1.391840
O	0.068396	-1.605477	-0.000010
O	2.550811	-1.382552	-1.391675
O	3.728741	0.600623	-0.000387
H	4.262372	0.363744	-0.773231
H	4.261693	0.365691	0.773518

For M=W (Figure S7b)

TS (**b**) ZPE=0.105284 E_{B,0K}=-1035.240072 E_{m,0K}=-1034.684246 E_{C,0K}=-1031.811485

W	-1.623760	-1.595295	0.141288
W	-1.243946	1.835047	0.068776
W	1.794678	-0.291842	-0.428067
O	-2.371675	-2.506144	-1.104117
O	-1.911748	-2.370877	1.644473
O	-2.235959	0.206987	0.161394
O	0.213409	-1.387189	-0.158307
O	-1.313940	2.707002	1.548160
O	-1.786502	2.851566	-1.203788
O	2.242747	-0.771468	-2.000498
O	0.494838	1.243684	-0.239556

O	3.048250	1.293101	-0.286333
O	2.829343	-1.134201	0.717216
H	2.652876	2.169300	-0.160282
C	4.734889	-0.680743	1.546419
H	4.281799	-0.984638	2.483396
H	5.106005	-1.479817	0.913653
C	5.056664	0.660234	1.287734
H	4.077558	1.026018	0.549854
H	4.996634	1.350584	2.128545
H	5.869826	0.836571	0.582965

W₃O₉·C₂H₄·H₂O (c)

ZPE=0.109124 E_{B,0K}=-1035.277519 E_{m,0K}=-1034.721828 E_{C,0K}=-1031.856443

W	-1.839090	-1.484070	-0.016183
W	-1.111815	1.920172	0.002786
W	1.669624	-0.488364	0.009325
O	-2.522117	-2.258046	-1.382518
O	-2.419326	-2.258170	1.396767
O	-2.234197	0.378509	0.005206
O	0.042430	-1.501840	-0.086312
O	-1.368092	2.902539	1.384901
O	-1.353510	2.874209	-1.400816
O	2.574854	-1.127191	-1.300771
O	0.615940	1.192036	0.026626
O	3.188197	1.147353	-0.061689
O	2.369167	-1.029084	1.476680
H	3.062144	1.878775	0.563062
C	5.758945	-0.636104	0.232650
H	5.818732	-0.822041	1.302398
H	5.252732	-1.386559	-0.369845
C	6.296226	0.463597	-0.322024
H	4.124461	0.831546	-0.003562
H	6.822316	1.204237	0.276435
H	6.256574	0.633983	-1.395478

W₃O₉·H₂O (d) ZPE=0.055986 E_{B,0K}=-956.6692335 E_{C,0K}=-953.4715147

W	-0.637787	1.963800	-0.000004
W	-1.628322	-1.374452	-0.000011
W	1.911994	-0.630475	0.000040
O	-0.825898	2.943932	1.388650
O	-0.826034	2.944041	-1.388560
O	-1.875859	0.512705	0.000016
O	1.041118	1.114181	-0.000113
O	-2.325778	-2.090247	-1.385907

O	-2.325913	-2.090358	1.385760
O	2.705694	-1.202748	1.408511
O	0.251084	-1.574162	0.000063
O	2.705777	-1.203267	-1.408179
O	3.690874	0.857849	-0.000481
H	4.242400	0.672986	-0.776021
H	4.241633	0.674940	0.776067

Alternative pathway for $M_3O_8(C_2H_5O)OH \rightarrow M_3O_9 + H_2O + C_2H_4$

For M=Mo (Figure S7)

Pathway 1

TS (b1) ZPE=0.104989 $E_{B,0K}=-1036.660668$ $E_{C,0K}=-1033.340031$

MO	-1.092027	1.952995	-0.022311
MO	-1.996558	-1.370527	0.148980
MO	1.607852	-0.518892	-0.197220
O	-1.169181	3.016752	1.296395
O	-1.389768	2.839295	-1.437790
O	-2.310357	0.529774	0.163287
O	0.598823	1.112378	-0.105499
O	-2.608008	-2.083191	-1.267562
O	-2.686226	-2.146908	1.493479
O	2.393338	-0.916668	1.323780
O	-0.155780	-1.424399	0.203534
O	1.668518	-1.927702	-1.483470
C	4.807238	0.036267	1.250662
C	4.801113	0.610640	-0.024487
H	3.609897	-0.465187	1.337352
H	5.395242	-0.874226	1.392518
H	5.248517	0.100567	-0.874374
H	4.592117	1.668911	-0.164217
O	2.976181	0.274138	-0.945409
H	2.396048	-1.883029	-2.118852
H	4.758560	0.713592	2.107730

$Mo_3O_8(OH)_2 \cdot C_2H_4$ (c1) ZPE=0.107802 $E_{B,0K}=-1036.691780$ $E_{C,0K}=-1033.372563$

MO	-1.371826	1.841214	0.154072
MO	-1.764092	-1.592607	0.265018
MO	1.563030	-0.150470	-0.660676
O	-1.313766	2.779659	1.562679
O	-2.080465	2.772784	-1.069531
O	-2.323114	0.252978	0.434500
O	0.387574	1.287842	-0.356224

O	-2.603491	-2.384569	-0.981767
O	-1.984621	-2.459913	1.708902
O	2.437517	-0.858474	0.816715
O	0.015609	-1.381670	-0.136227
O	1.473621	-1.190303	-2.238061
C	5.353781	-0.434157	1.977960
C	5.352785	0.507539	1.024602
H	3.362434	-0.573948	1.001985
H	5.719232	-1.444072	1.784996
H	5.714546	0.304235	0.015947
H	5.009040	1.523688	1.223244
O	2.852181	0.783498	-1.235966
H	2.115540	-0.964468	-2.927683
H	5.012747	-0.222144	2.992594

Mo₃O₈(OH)₂·C₂H₄(**d1**) ZPE=0.054510 E_{B,0K}=-958.091279 E_{C,0K}=-954.993178

MO	1.163478	1.761805	0.014147
MO	1.265870	-1.690174	0.005599
MO	-2.024784	-0.076316	-0.124493
O	1.701738	2.775511	-1.230961
O	1.416588	2.547877	1.496210
O	2.012074	0.055701	-0.026513
O	-0.639551	1.301132	-0.190491
O	1.546197	-2.459490	1.488060
O	1.884557	-2.671371	-1.226572
O	-2.789809	-0.270644	-1.598668
O	-0.567408	-1.318906	-0.246364
O	-2.728150	-1.297628	1.149541
O	-3.139040	1.282263	0.581269
H	-3.632217	-1.168145	1.468655
H	-2.937000	1.809345	1.366640

TS (**e**) ZPE=0.051759 E_{B,0K}=-958.062249 E_{C,0K}=-954.968624

MO	-0.834488	1.909988	0.007865
MO	-1.537513	-1.499325	-0.062826
MO	1.912755	-0.450954	0.137707
O	-1.086605	2.837029	1.400396
O	-1.125862	2.895166	-1.338195
O	-1.937377	0.351842	-0.010536
O	0.901986	1.197352	-0.055052
O	-2.156622	-2.231832	-1.455077
O	-2.173447	-2.310698	1.276287
O	2.355249	-0.557397	1.750921
O	0.365229	-1.523204	-0.060842
O	3.104073	-1.402275	-0.822791

O	3.342270	0.804457	-0.805251
H	3.539108	-0.375509	-1.226165
H	3.038081	1.584177	-1.288049

Pathway 2

TS(**b2**) ZPE=0.104492 E_{B,0K}=-1036.645150 E_{C,0K}=-1033.326754

MO	-0.035468	1.961465	-0.388757
MO	2.279969	-0.388238	0.402075
MO	-1.098937	-1.505365	-0.502306
O	-0.100532	3.247327	-1.497997
O	-0.888696	2.386329	1.050878
O	1.736888	1.404867	-0.000789
O	-0.789482	0.444395	-1.060925
O	2.332838	-0.623390	2.088161
O	3.791801	-0.782814	-0.264879
O	-1.593528	-2.087935	-2.004440
O	0.912297	-1.385793	-0.340237
O	-0.833970	-3.077590	0.543461
O	-2.506281	-0.989436	0.414808
H	0.002462	-3.555834	0.473054
C	-3.194166	0.647465	2.073473
H	-2.303606	1.255232	1.857682
H	-3.101719	-0.170308	2.789891
C	-4.394735	0.868109	1.389518
H	-3.859909	0.071882	0.666809
H	-5.307223	0.380919	1.737603
H	-4.500947	1.786762	0.810189

Mo₃O₈(OH)₂·C₂H₄(**c2**) ZPE=0.107190 E_{B,0K}=-1036.700038 E_{C,0K}=-1033.379346

MO	0.200223	2.013396	-0.377051
MO	2.229846	-0.603131	0.518140
MO	-1.169461	-1.359653	-0.651062
O	0.378161	3.174566	-1.596918
O	-0.581556	2.729705	0.952259
O	1.852818	1.227758	0.130418
O	-0.774019	0.523388	-0.957110
O	2.291818	-0.881679	2.192360
O	3.684539	-1.130032	-0.172494
O	-1.210768	-2.148522	-2.125418
O	0.751964	-1.467209	-0.224376
O	-1.317651	-2.633172	0.755517
O	-2.947988	-0.921420	-0.373678
H	-0.512146	-3.074318	1.058337
C	-4.258506	0.292184	2.312037

H	-5.203671	-0.245181	2.217814
H	-3.541104	-0.102608	3.033512
C	-4.004077	1.399710	1.602113
H	-3.328082	-0.399506	0.368720
H	-4.734612	1.805205	0.899963
H	-3.068963	1.952295	1.711119

For M=W (Figure S8)

Pathway 1

TS (b1) ZPE=0.104733 E_{B,0K}=-1035.241056 E_{C,0K}=-1031.81093

W	-0.938538	1.941648	-0.027461
W	-1.867874	-1.369570	0.131843
W	1.772102	-0.548525	-0.202921
O	-0.971099	2.978745	1.335360
O	-1.251243	2.869766	-1.432563
O	-2.182187	0.526192	0.151311
O	0.734888	1.087529	-0.162362
O	-2.552165	-2.098387	-1.262244
O	-2.489384	-2.140567	1.532163
O	2.485259	-0.892253	1.373426
O	-0.019138	-1.439607	0.089088
O	1.960618	-2.021702	-1.395290
C	4.872811	0.160067	1.457167
C	4.931889	0.724923	0.181234
H	3.705127	-0.390886	1.450767
H	5.493931	-0.718713	1.649916
H	5.444417	0.225453	-0.637441
H	4.665233	1.765114	0.009022
O	3.153324	0.287258	-0.894178
H	2.721304	-2.029584	-1.990187
H	4.729737	0.839983	2.301690

W₃O₈(OH)₂·C₂H₄ (c1) ZPE=0.107589 E_{B,0K}=-1035.271878 E_{C,0K}=-1031.843547

W	-1.239967	1.820183	0.128864
W	-1.609581	-1.610038	0.204898
W	1.763196	-0.139416	-0.571664
O	-1.248501	2.748290	1.565309
O	-1.900750	2.764561	-1.134099
O	-2.207033	0.218850	0.352130
O	0.536631	1.284764	-0.301271
O	-2.401473	-2.430943	-1.076113
O	-1.845080	-2.481950	1.663015
O	2.562972	-0.887276	0.926450

O	0.185479	-1.375581	-0.154008
O	1.795565	-1.159271	-2.158723
C	5.453323	-0.608186	2.157337
C	5.306761	0.598880	1.593960
H	3.469255	-0.611912	1.198922
H	5.921497	-1.436255	1.622470
H	5.641413	0.804195	0.576473
H	4.861301	1.432748	2.139057
O	3.064523	0.865430	-1.032476
H	2.462462	-0.937234	-2.824065
H	5.134914	-0.804620	3.182402

W₃O₈(OH)₂ (d1) ZPE=0.053764 E_{B,0K}=-956.6725799 E_{C,0K}=-953.4666443

W	1.249348	-1.680518	-0.000002
W	1.121706	1.761226	-0.019546
W	-2.096914	-0.054295	0.046811
O	1.743153	-2.610665	1.349105
O	1.660105	-2.524286	-1.433352
O	2.000606	0.076103	0.022557
O	-0.586860	-1.337290	0.049865
O	1.531663	2.650567	-1.422135
O	1.496686	2.704433	1.356732
O	-2.594551	-0.144909	1.656548
O	-0.702094	1.283733	-0.040296
O	-3.290699	1.169494	-0.713042
O	-2.968003	-1.430781	-0.915892
H	-4.001355	1.676243	-0.301205
H	-2.605079	-2.321953	-0.997015

TS (e) ZPE=0.051054 E_{B,0K}=-956.631774 E_{C,0K}=-953.4305155

W	-0.863788	1.887360	0.001745
W	-1.442894	-1.544689	-0.038261
W	1.982325	-0.381030	0.084796
O	-1.212102	2.866778	1.357991
O	-1.120552	2.809856	-1.413957
O	-1.918776	0.293415	-0.013348
O	0.894500	1.223581	0.070165
O	-2.067261	-2.334960	-1.416564
O	-2.018693	-2.352432	1.350812
O	2.541568	-0.567793	1.673352
O	0.459804	-1.508248	-0.074878
O	3.142946	-1.235913	-1.003668
O	3.354498	0.978701	-0.795883
H	3.700946	-0.182874	-1.148024
H	3.854044	1.637522	-0.296879

Pathway 2

TS (b2) ZPE=0.104376 E_{B,0K}=-1035.224913 E_{C,0K}=-1031.796531

W	0.004749	1.960753	-0.289449
W	2.182918	-0.585609	0.302785
W	-1.378600	-1.392572	-0.375528
O	-0.013278	3.269693	-1.397539
O	-0.758114	2.433295	1.199519
O	1.746769	1.261047	0.018101
O	-0.910235	0.514975	-0.939313
O	2.490013	-0.882103	1.966455
O	3.538364	-1.085691	-0.620955
O	-1.949963	-1.936814	-1.882984
O	0.634866	-1.457447	-0.226306
O	-1.272729	-2.986925	0.662625
O	-2.735834	-0.752029	0.564907
H	-0.542252	-3.608267	0.554156
C	-3.243972	0.919410	2.224854
H	-2.312583	1.454494	1.991754
H	-3.200353	0.097771	2.941102
C	-4.440864	1.236105	1.571503
H	-3.996584	0.399166	0.834371
H	-5.379444	0.826413	1.948837
H	-4.489579	2.163027	0.997713

W₃O₈(OH)₂·C₂H₄ (c2) ZPE=0.106834 E_{B,0K}=-1035.280592 E_{C,0K}=-1031.850947

W	0.149220	2.007963	-0.296217
W	2.138741	-0.709235	0.383219
W	-1.414735	-1.327523	-0.455367
O	0.280797	3.098004	-1.608017
O	-0.473341	2.842204	1.068562
O	1.800847	1.149942	0.105264
O	-0.966750	0.564437	-0.704378
O	2.485823	-1.041850	2.027982
O	3.429500	-1.284660	-0.581274
O	-1.548610	-2.027899	-1.986556
O	0.515313	-1.499717	-0.104561
O	-1.571431	-2.709198	0.834629
O	-3.153051	-0.803847	-0.083067
H	-0.829799	-3.287689	1.054032
C	-4.349282	0.693149	2.501858
H	-3.679258	0.281753	3.258865
H	-5.342609	0.246428	2.432766
C	-3.982663	1.719968	1.722842

H	-3.503387	-0.219345	0.624276
H	-4.665940	2.145766	0.985963
H	-2.998818	2.185911	1.806198



For M=Mo (Figure S9a)

TS (b) ZPE=0.10776 $E_{\text{B},0\text{K}}=-1036.68577$ $E_{\text{C},0\text{K}}=-1033.370382$

MO	0.009125	1.972805	-0.236877
MO	2.384233	-0.486074	0.313404
MO	-1.022203	-1.466362	-0.352611
O	0.013302	3.140034	-1.463153
O	-0.679883	2.662302	1.151585
O	1.755847	1.292136	0.140860
O	-0.931690	0.445551	-0.756747
O	3.142862	-0.739340	1.802986
O	3.494814	-0.863798	-0.904230
O	-1.188486	-2.117420	-1.889973
O	0.801857	-1.532988	0.159358
O	-1.763735	-2.692690	0.738789
O	-2.787106	-0.768199	0.547889
H	-2.650985	-1.941032	0.974374
C	-3.830059	0.163661	0.211475
H	-3.442086	0.837705	-0.563068
H	-4.666584	-0.407161	-0.217965
C	-4.262543	0.940873	1.444224
H	-5.071582	1.634158	1.173712
H	-4.636944	0.264364	2.224059
H	-3.427004	1.524524	1.851351

$\text{Mo}_3\text{O}_9 \cdot \text{C}_2\text{H}_5\text{OH}$ (c) ZPE=0.112948 $E_{\text{B},0\text{K}}=-1036.730044$ $E_{\text{C},0\text{K}}=-1033.420663$

MO	0.714207	2.031548	-0.007232
MO	2.307475	-1.049091	0.030346
MO	-1.321761	-1.003274	-0.065257
O	0.717072	2.965045	-1.422640
O	0.700697	3.087421	1.319778
O	2.205515	0.849172	0.044627
O	-0.775577	0.899103	0.042082
O	2.986805	-1.635643	1.466597
O	3.242802	-1.616334	-1.262012
O	-2.010045	-1.740565	-1.426571
O	0.507937	-1.570080	-0.143301
O	-1.921222	-1.765465	1.325778
O	-3.219413	0.220409	-0.065770

H	-3.096979	1.046882	0.423276
C	-4.522423	-0.375798	0.225670
H	-4.600897	-1.206058	-0.483010
H	-4.494516	-0.781630	1.245441
C	-5.630007	0.641713	0.036365
H	-6.597368	0.161151	0.236592
H	-5.527963	1.483792	0.736819
H	-5.640933	1.030164	-0.989866

For M=W (Figure S9b)

TS (b) ZPE=0.10731 E_{B,0K}=-1035.25761 E_{C,0K}=-1031.83090

W	-0.269714	2.034722	0.086449
W	-2.189935	-0.851980	-0.180013
W	1.396398	-1.201894	0.234689
O	-0.306551	3.090395	1.430696
O	0.013976	2.960662	-1.323781
O	-1.880851	1.019577	-0.070092
O	1.049579	0.717155	0.293793
O	-2.954656	-1.274000	-1.647549
O	-3.165780	-1.395791	1.111301
O	1.718828	-1.639876	1.840738
O	-0.443462	-1.592808	-0.085415
O	2.182487	-2.445388	-0.813598
O	3.187139	-0.490683	-0.558854
H	3.105529	-1.674550	-0.951956
C	4.199412	0.409801	-0.064302
H	3.683114	1.273230	0.375517
H	4.758374	-0.103173	0.732214
C	5.113608	0.836881	-1.198873
H	5.880666	1.522154	-0.811774
H	5.621382	-0.029931	-1.642768
H	4.547726	1.355500	-1.983378

W₃O₉•C₂H₅OH (c) ZPE=0.112711 E_{B,0K}=-1035.297708 E_{C,0K}=-1031.877291

W	0.618812	2.021697	-0.001392
W	2.102859	-1.111882	0.006347
W	-1.541421	-0.950041	-0.022513
O	0.644525	2.986600	-1.415263
O	0.633361	3.055447	1.363740
O	2.075810	0.792739	0.027641
O	-0.912162	0.940122	0.025093
O	2.819588	-1.733328	1.429166
O	2.965137	-1.710847	-1.343313
O	-2.246647	-1.744074	-1.364785

O	0.278992	-1.562591	-0.094510
O	-2.130414	-1.673388	1.412466
O	-3.355798	0.309013	-0.060649
H	-3.242948	1.149924	0.406258
C	-4.690374	-0.260146	0.177146
H	-4.753201	-1.087203	-0.536019
H	-4.703812	-0.663405	1.197322
C	-5.758144	0.787855	-0.056493
H	-6.744371	0.332583	0.106814
H	-5.662124	1.627676	0.647517
H	-5.720081	1.173294	-1.083116



For M=Mo (Figure S10)

Pathway 1

TS (b1) ZPE=0.163231 $E_{\text{B},0\text{K}}=-1115.286602$ $E_{\text{m},0\text{K}}=-1114.636281$ $E_{\text{C},0\text{K}}=-1111.757327$

MO	-2.006510	-1.299863	0.058512
MO	-1.259188	1.980353	0.228365
MO	1.452322	-0.338269	-0.820800
O	-2.675299	-1.493517	-1.484260
O	-2.679947	-2.477618	1.070259
O	-2.326739	0.416375	0.718652
O	-0.063172	-1.559671	-0.012111
O	-0.664469	2.732249	1.634041
O	-2.095928	3.112329	-0.723031
O	1.662402	-0.611521	-2.459394
O	0.034428	1.076024	-0.706391
O	2.625759	0.998895	-0.180785
O	2.343353	-1.821662	-0.020187
C	2.011065	-2.691174	0.940781
H	2.323064	-3.715217	0.724222
H	0.505063	-2.365727	0.496201
C	2.040291	-2.236998	2.382768
H	1.543250	-1.270880	2.521387
H	1.546180	-2.977720	3.017526
H	3.076015	-2.131289	2.736467
C	4.046841	0.932325	0.021578
C	4.456735	1.918397	1.109668
H	4.536344	1.177529	-0.929085
H	4.328905	-0.094892	0.292810
H	5.542886	1.886392	1.248259
H	4.170848	2.936512	0.832746

H	3.976517	1.671644	2.061121
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Mo₃O₇(OC₂H₅)(OH)•CH₃CH=O (c1)

ZPE=0.166267 E_{B,0K}=-1115.301702 E_{m,0K}=-1114.657678 E_{C,0K}=-1111.768481

MO	-2.094806	-1.197667	-0.016696
MO	-1.273688	1.858103	0.317304
MO	1.387326	-0.545596	-0.734901
O	-2.615588	-1.253363	-1.624890
O	-2.892731	-2.438458	0.816495
O	-2.548849	0.431449	0.772084
O	-0.169707	-1.800770	0.142616
O	-0.551072	2.480969	1.728147
O	-1.938862	3.107786	-0.625970
O	1.638147	-0.868079	-2.357945
O	-0.196018	0.676885	-0.617937
O	2.364320	1.006437	-0.127512
O	2.658123	-1.750045	0.228485
C	3.120301	-2.171925	1.323543
H	3.826343	-3.006824	1.266597
H	0.003129	-2.702879	0.455329
C	2.785595	-1.583145	2.657009
H	2.063478	-0.768646	2.572806
H	2.397274	-2.354872	3.333650
H	3.699785	-1.193435	3.124783
C	3.751070	1.157149	0.176824
C	4.300073	2.397922	-0.525812
H	4.322478	0.271507	-0.134950
H	3.861328	1.267202	1.266052
H	5.356860	2.541697	-0.272818
H	4.211604	2.293761	-1.611182
H	3.742447	3.286758	-0.217941

Mo₃O₇(OC₂H₅)(OH) (d1)

ZPE=0.108755 E_{B,0K}=-961.422622 E_{m,0K}=-960.874628 E_{C,0K}=-958.267852

MO	2.015177	-0.906323	-0.400876
MO	0.531828	1.916869	0.232739
MO	-1.583846	-1.150751	0.521520
O	2.685623	-1.278535	1.108354
O	2.927454	-1.684913	-1.597658
O	1.987035	0.927491	-0.666855
O	0.180877	-1.769911	-0.536003
O	-0.360778	2.845520	-0.888493
O	1.066213	2.848965	1.552536
O	-1.744426	-1.987409	1.967396

O	-0.387742	0.389900	0.727516
O	-3.098216	-0.787403	-0.479032
H	0.125710	-2.613766	-1.011887
C	-3.766422	-0.066617	-1.532620
C	-3.995851	1.388775	-1.139268
H	-4.715604	-0.582974	-1.708951
H	-3.157063	-0.137904	-2.441244
H	-4.552906	1.894271	-1.934911
H	-4.579225	1.450081	-0.216363
H	-3.048253	1.916296	-0.999528

Pathway 2

TS (b2) ZPE=0.163642 $E_{B,0K}=-1115.294074$ $E_{m,0K}=-1114.640023$ $E_{C,0K}=-1111.755977$

MO	1.831444	-1.489057	-0.628381
MO	1.523024	1.689022	0.661089
MO	-1.540863	-0.170378	-0.108586
O	2.389711	-2.758216	0.350707
O	2.287274	-1.807820	-2.232206
O	2.490369	0.178674	-0.050354
O	-0.046813	-1.306255	-0.477052
O	2.065979	3.182789	0.053097
O	1.628839	1.706554	2.359641
O	-2.008492	-0.075648	1.633306
O	-0.189593	1.318822	0.096162
O	-2.511785	0.937604	-1.194699
O	-2.791746	-1.590473	-0.026045
C	-3.328598	-2.118434	1.084427
H	-2.765639	-0.907020	1.833399
H	-4.422894	-2.106253	1.090251
C	-2.655551	-3.317439	1.709426
H	-3.055963	-3.482136	2.713835
H	-2.852829	-4.220614	1.116328
H	-1.572408	-3.182594	1.773624
C	-2.464330	2.253083	-1.791867
C	-3.606352	3.111866	-1.267234
H	-2.533865	2.105392	-2.874277
H	-1.487071	2.683399	-1.548753
H	-3.563583	4.095756	-1.746054
H	-4.574831	2.657688	-1.494408
H	-3.523283	3.251012	-0.186057

Mo₃O₇(OC₂H₅)(OH)·CH₃CH=O (c2)

ZPE=0.16676 $E_{B,0K}=-1115.321597$ $E_{m,0K}=-1114.671052$ $E_{C,0K}=-1111.771722$

MO	1.346223	1.597582	0.939255
MO	1.844076	-1.356742	-0.669189

MO	-1.564278	-0.253743	-0.277893
O	1.825504	3.077287	0.240615
O	1.391841	1.725855	2.637260
O	2.445671	0.164245	0.333897
O	-0.367133	1.139174	0.358821
O	2.624337	-2.802567	-0.217435
O	2.054708	-1.058104	-2.341533
O	-1.573166	-0.302977	-2.183664
O	0.034247	-1.416127	-0.305440
O	-2.488229	-1.328455	0.856997
O	-2.957312	1.192141	-0.490184
C	-3.232268	2.287921	-1.025175
H	-0.878373	-0.859949	-2.578164
H	-4.192035	2.738638	-0.744331
C	-2.347815	3.010848	-1.985325
H	-2.013865	3.950916	-1.525755
H	-1.483994	2.411313	-2.268594
H	-2.923283	3.283319	-2.877988
C	-2.663819	-2.665082	1.374207
C	-2.868207	-2.620073	2.881614
H	-1.765990	-3.230682	1.102677
H	-3.528001	-3.098439	0.861276
H	-3.002416	-3.640514	3.255212
H	-1.999559	-2.181159	3.379035
H	-3.756458	-2.036945	3.138772

Mo₃O₇(OC₂H₅) (OH) (d2)

ZPE=0.108363 E_{B,0K}=-961.4341988 E_{m,0K}=-960.8818564 E_{C,0K}=-958.2679467

MO	1.272812	1.691320	-0.004711
MO	1.328372	-1.612394	0.302807
MO	-1.650074	-0.171783	-0.817961
O	1.772218	2.227807	-1.541528
O	1.526756	2.910313	1.150927
O	2.207543	0.082761	0.440648
O	-0.545449	1.189876	-0.083954
O	0.708648	-2.035726	1.834221
O	2.361476	-2.828758	-0.277321
O	-2.357278	-0.527805	-2.501115
O	-0.140831	-1.335811	-0.846326
O	-3.071128	0.005904	0.315742
H	-2.028547	-0.262763	-3.374168
C	-3.359887	-0.279060	1.707781
C	-3.388077	1.014966	2.511690
H	-2.600962	-0.974392	2.082875
H	-4.331909	-0.781652	1.716784

H	-3.627012	0.782493	3.554394
H	-2.416931	1.515515	2.483708
H	-4.149110	1.696890	2.123572

Pathway 3

TS **(b3)** ZPE=0.163517 E_{B,0K}=-1115.288875 E_{m,0K}=-1114.639034 E_{C,0K}=
-1111.755155

MO	0.275661	2.146389	0.235763
MO	2.409045	-0.781563	0.112643
MO	-0.919472	-1.006316	-0.872962
O	0.618881	3.692099	-0.368233
O	-0.092509	2.222444	1.898594
O	1.900131	1.003246	0.212971
O	-0.292303	0.682848	-1.085843
O	2.770368	-1.400923	1.654281
O	3.759168	-1.006983	-0.891884
O	-1.434124	-1.714989	-2.308076
O	0.838894	-1.644670	-0.588457
O	-1.597828	-1.767034	0.684455
O	-2.736261	0.211044	-0.724173
C	-2.920478	1.105627	0.151993
H	-1.504480	2.194459	-0.045759
H	-2.546796	0.943781	1.172185
C	-3.984293	2.146528	-0.044703
H	-4.938588	1.704312	0.273347
H	-3.791981	3.025034	0.573405
H	-4.065957	2.423360	-1.096701
C	-2.687052	-2.612829	1.106615
C	-2.602249	-2.837879	2.610238
H	-2.618293	-3.558232	0.558115
H	-3.624824	-2.118428	0.826653
H	-3.427515	-3.483927	2.927271
H	-1.659346	-3.322033	2.876172
H	-2.672980	-1.891127	3.152710

Mo₃O₈(OC₂H₅)(H)·CH₃CH=O **(c3)**

ZPE=0.162954 E_{B,0K}=-1115.29629 E_{m,0K}=-1114.645566

MO	1.744559	1.889431	0.137354
MO	1.704132	-1.823107	0.084538
MO	-1.384345	-0.401617	-0.729129
O	3.289751	2.580988	0.060150
O	1.005619	2.489382	1.543390
O	2.149235	-0.023260	0.058906
O	-0.274871	0.952070	-0.566792

O	1.800765	-2.481361	1.648907
O	2.680695	-2.742088	-0.956958
O	-1.927399	-0.633625	-2.312885
O	-0.111260	-1.772108	-0.511766
O	-2.520222	-0.848775	0.678745
O	-3.047713	1.335876	-0.822887
C	-3.230776	2.466067	-0.368833
H	-4.133744	3.002011	-0.713961
H	1.139369	2.875544	-1.121840
C	-2.366281	3.190625	0.608565
H	-1.507145	2.612005	0.940421
H	-2.026638	4.124878	0.142858
H	-2.989848	3.487743	1.461715
C	-3.845531	-1.369535	0.894667
C	-4.021144	-1.719436	2.366829
H	-3.983521	-2.251894	0.260150
H	-4.561942	-0.602909	0.578118
H	-5.030465	-2.111682	2.529901
H	-3.298871	-2.480691	2.672530
H	-3.884131	-0.835834	2.996196

Mo₃O₇(OC₂H₅)(OH) (**d3**)

ZPE=0.105294 E_{B,0K}=-961.432287 E_{m,0K}=-960.877560 E_{C,0K}=-958.2770283

MO	-1.986632	-1.622357	0.023448
MO	-0.945359	1.940555	0.205138
MO	1.663447	-0.157016	-0.721277
O	-3.650684	-1.900593	0.128320
O	-1.274924	-2.404599	1.343606
O	-1.821359	0.320787	-0.037491
O	0.325854	-1.248602	-0.858535
O	-1.023114	2.479555	1.810981
O	-1.565475	3.153881	-0.802345
O	2.464821	-0.055867	-2.208299
O	0.868137	1.479218	-0.263807
O	2.834414	-0.710092	0.585947
H	-1.730733	-2.646156	-1.319804
C	4.195630	-1.148625	0.806897
C	4.798783	-0.386933	1.979294
H	4.763443	-0.988104	-0.115507
H	4.144453	-2.222251	1.012548
H	5.815977	-0.751062	2.156464
H	4.847261	0.684764	1.768112
H	4.210602	-0.542928	2.887079

Pathway 4

TS (b4) ZPE=0.163693 E_{B,0K}=-1115.283948 E_{m,0K}=-1114.639173 E_{C,0K}=-1111.751797

MO	-1.892468	-1.470626	-0.309220
MO	-1.354735	1.921642	0.255768
MO	1.475744	-0.102126	-0.525031
O	-2.753366	-2.043170	-1.655267
O	-2.174122	-2.528151	0.996567
O	-2.369999	0.328548	0.123950
O	-0.080806	-1.335572	-0.673413
O	-1.226169	2.459866	1.857249
O	-2.047716	3.174683	-0.649913
O	1.995538	-0.324867	-2.116175
O	0.314318	1.421927	-0.498570
O	3.083389	0.631424	0.061012
O	0.952587	-0.132736	1.654591
C	1.673951	-1.177287	1.853038
H	2.735816	-1.015645	2.100288
H	2.066301	-1.576234	0.343489
C	1.087123	-2.480958	2.327465
H	0.098835	-2.669064	1.909670
H	1.762850	-3.315733	2.125676
H	0.985293	-2.383923	3.417318
C	5.398380	-0.148776	0.134472
C	4.384592	0.776511	-0.529927
H	5.123568	-1.197775	-0.009958
H	6.381987	0.010638	-0.318982
H	5.474716	0.057865	1.205606
H	4.660166	1.826986	-0.382524
H	4.298253	0.577005	-1.604832

Mo₃O₈(OC₂H₅)(H)·CH₃CH=O (c4)

ZPE=0.163787 E_{B,0K}=-1115.307667 E_{m,0K}=-1114.663481 E_{C,0K}=-1111.775967

MO	-2.153352	-0.926342	-0.036287
MO	-0.470283	2.091498	0.041907
MO	1.303814	-0.837650	-1.110013
O	-3.540974	-1.329169	-0.924000
O	-2.200536	-1.747903	1.463061
O	-1.984257	0.950170	0.236360
O	-0.606241	-1.314251	-0.981046
O	0.145181	2.620574	1.539178
O	-0.871521	3.467099	-0.862587
O	1.584463	-1.291051	-2.696430
O	0.740818	1.033588	-0.918161
O	3.002865	-0.638978	-0.444719

O	0.666558	-0.410875	1.466123
C	0.384325	-0.795505	2.600735
H	-0.200494	-0.123351	3.253184
H	1.342635	-2.331715	-0.302583
C	0.760556	-2.124361	3.171817
H	1.261703	-1.983988	4.136789
H	1.382560	-2.700021	2.485860
H	-0.170894	-2.668929	3.371974
C	3.900654	-0.598447	0.666485
C	4.172833	0.849688	1.069533
H	4.819502	-1.103361	0.350347
H	3.451794	-1.160755	1.491298
H	4.888233	0.861074	1.898324
H	4.602413	1.408265	0.234108
H	3.253971	1.345609	1.391506

W₃O₈(OC₂H₅) (H) (d4)

ZPE=0.106443 E_{B,0K}=-961.439321 E_{m,0K}=-960.8872602 E_{C,0K}=-958.2811529

MO	-1.835298	-1.250572	0.331345
MO	-0.688949	1.958741	-0.213479
MO	1.615621	-0.842679	-0.653582
O	-3.096592	-2.149457	-0.357560
O	-1.735324	-1.613128	1.988806
O	-2.020106	0.631507	0.067407
O	-0.192012	-1.561393	-0.504016
O	-0.294467	2.757716	1.234669
O	-1.144285	3.113123	-1.368353
O	2.169018	-1.588246	-2.047350
O	0.761768	0.911634	-0.777009
O	3.138887	-0.223429	0.164517
H	1.744212	-2.010834	0.564924
C	3.769773	0.090733	1.416110
C	2.777540	0.497880	2.498275
H	4.475610	0.897388	1.190369
H	4.345377	-0.795953	1.705091
H	3.326259	0.747148	3.411902
H	2.198886	1.376284	2.198924
H	2.092969	-0.322855	2.733655

Pathway 5

TS (b5) ZPE=0.162306 E_{B,0K}=-1115.282408 E_{m,0K}=-1114.629179 E_{C,0K}=-1111.745493

MO	-2.319640	-0.572676	-0.221059
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MO	-0.392287	2.266910	0.301437
MO	1.336655	-0.766487	-0.491059
O	-3.736512	-0.670963	-1.143317
O	-2.330661	-1.806541	1.121800
O	-1.978307	1.181708	0.386406
O	-0.906267	-0.885448	-1.203130
O	0.124411	2.659008	1.871332
O	-0.616806	3.701493	-0.574299
O	1.730872	-1.615958	-1.890043
O	0.821113	1.123878	-0.540661
O	3.025247	-0.346010	0.235253
O	0.791357	-1.842954	0.900993
C	0.112076	-2.776815	1.595399
H	0.108033	-2.542184	2.664697
H	-1.363030	-2.280108	1.371320
C	0.302078	-4.211203	1.173580
H	-0.372236	-4.854345	1.746257
H	0.082311	-4.343623	0.109214
H	1.331553	-4.553502	1.350992
C	4.025854	0.435337	-0.445582
C	5.236742	0.608326	0.463183
H	3.595157	1.409723	-0.712243
H	4.300295	-0.084496	-1.373846
H	6.001159	1.200864	-0.050470
H	4.956270	1.125744	1.384698
H	5.665837	-0.363014	0.723810

Mo₃O₇(OC₂H₅)(OH)·CH₃CH=O (c5)

ZPE=0.165096 E_{B,0K}=-1115.316034 E_{m,0K}=-1114.667845 E_{C,0K}=-1111.777663

MO	-1.965106	-1.435686	-0.036801
MO	-1.351869	1.880025	0.253084
MO	1.398746	-0.184891	-0.756579
O	-2.694385	-2.087683	-1.409641
O	-2.254630	-2.525836	1.483493
O	-2.544080	0.301450	0.289983
O	-0.187631	-1.264796	-0.353243
O	-0.884911	2.191579	1.868007
O	-2.109212	3.243677	-0.434739
O	1.827446	-0.167846	-2.378467
O	0.072214	1.301794	-0.739000
O	2.333845	0.704911	0.661942
O	2.637219	-1.856247	-0.325361
C	3.069195	-2.571991	0.593637
H	3.655881	-3.454526	0.299400
H	-1.641693	-2.637988	2.225811

C	2.844793	-2.335711	2.052831
H	2.279547	-1.421878	2.234466
H	2.330834	-3.206172	2.481841
H	3.815625	-2.274462	2.560570
C	3.663691	1.196557	0.815367
C	3.856998	2.540170	0.112726
H	4.386994	0.461713	0.430341
H	3.837341	1.307306	1.893335
H	4.872566	2.911446	0.288770
H	3.709978	2.440179	-0.967282
H	3.143477	3.275372	0.493996

Mo₃O₇(OC₂H₅) (OH) (d5)

ZPE=0.107562 E_{B,0K}=-961.4460325 E_{m,0K}=-960.8936533 E_{C,0K}=-958.2912759

MO	-2.010252	-0.911458	0.371305
MO	-0.362087	1.955803	-0.206903
MO	1.412982	-1.019760	-0.785808
O	-3.161560	-1.600563	-0.643553
O	-2.198269	-1.511641	2.156356
O	-1.968781	0.962355	0.290311
O	-0.349720	-1.457823	-0.182158
O	0.489827	2.309874	1.235598
O	-0.704898	3.360199	-1.102249
O	1.789732	-1.881737	-2.180232
O	0.634945	0.713087	-1.172175
O	2.711235	-0.868957	0.530503
H	-1.542653	-2.013237	2.665404
C	2.998302	-0.278934	1.820554
C	4.411434	0.288596	1.826052
H	2.893137	-1.080795	2.560115
H	2.258788	0.501827	2.028794
H	4.629693	0.707188	2.814046
H	5.145362	-0.491263	1.605778
H	4.510186	1.087393	1.086066

For M=W (Figure S11)

Pathway 1

TS (b1) ZPE=0.163886 E_{B,0K}=-1113.862672 E_{m,0K}=-1113.248621

W	-1.752519	-1.483355	-0.205329
W	-1.180896	1.920041	0.191606
W	1.660683	-0.196715	-0.411343

O	-2.596294	-2.133271	-1.550273
O	-2.054130	-2.473506	1.169601
O	-2.231591	0.338940	0.113727
O	0.072142	-1.389945	-0.538840
O	-1.110028	2.544505	1.785194
O	-1.807665	3.141120	-0.833407
O	2.164693	-0.463694	-2.018123
O	0.516073	1.356907	-0.423624
O	3.253565	0.580239	0.141875
O	1.162953	-0.225288	1.740833
C	1.870333	-1.282875	1.952437
H	2.930760	-1.133595	2.207924
H	2.277224	-1.692329	0.429579
C	1.258503	-2.571350	2.428391
H	0.265991	-2.740313	2.011776
H	1.919089	-3.419213	2.231588
H	1.157772	-2.467394	3.518145
C	5.622173	-0.007662	0.244551
C	4.543470	0.807598	-0.458167
H	5.430608	-1.080142	0.143099
H	6.592332	0.209074	-0.213933
H	5.677876	0.248023	1.306589
H	4.734249	1.881360	-0.356870
H	4.471636	0.554378	-1.521959

W₃O₈(OC₂H₅) (H)•CH₃CH=O (c1)

ZPE=0.164079 E_{B,0K}=-1113.884691 E_{m,0K}=-1113.268673 E_{C,0K}=-1110.241436

W	-1.701247	-1.466490	-0.144434
W	-1.145122	1.886941	0.033279
W	1.733190	-0.343309	-0.715952
O	-2.674687	-2.532397	-1.072377
O	-1.724906	-1.942051	1.514432
O	-2.245903	0.359302	-0.277539
O	0.050449	-1.385287	-0.732589
O	-1.213430	2.338748	1.695536
O	-1.576184	3.227726	-0.947687
O	2.069392	-0.407030	-2.371017
O	0.552512	1.237211	-0.349253
O	3.295375	0.336054	-0.053711
O	1.409199	-0.661788	1.743722
C	0.641622	-0.470979	2.691118
H	-0.188261	0.247648	2.598346
H	2.301462	-1.901021	-0.291307
C	0.772215	-1.168148	4.004246
H	0.800275	-0.426550	4.811287

H	1.651530	-1.812407	4.032333
H	-0.137688	-1.762539	4.154983
C	4.288883	0.533127	0.956974
C	5.656361	0.085049	0.456072
H	3.979269	-0.020869	1.847928
H	4.280017	1.604116	1.187301
H	6.402198	0.261919	1.237846
H	5.650501	-0.981690	0.217242
H	5.946960	0.644660	-0.436602

W₃O₈(OC₂H₅) (H) (**d1**)

ZPE=0.106277 E_{B,0K}=-960.0113752 E_{m,0K}=-959.489736 E_{C,0K}=-956.742555

W	-1.825845	-1.227293	0.269721
W	-0.592792	1.969878	-0.172352
W	1.746567	-0.870603	-0.442431
O	-2.983846	-2.087623	-0.654939
O	-1.992723	-1.654708	1.922805
O	-1.961794	0.663123	0.045953
O	-0.073898	-1.547742	-0.312674
O	-0.336291	2.858953	1.273899
O	-0.927779	3.060888	-1.451299
O	2.273412	-1.618358	-1.866631
O	0.908872	0.907799	-0.533781
O	3.292426	-0.209924	0.283332
H	1.911231	-2.071349	0.761053
C	4.076902	0.229695	1.403676
C	3.217121	0.712376	2.565285
H	4.721796	1.025969	1.018920
H	4.709287	-0.617045	1.689910
H	3.868318	1.045189	3.379480
H	2.585146	1.554218	2.269439
H	2.586261	-0.095351	2.948693

Pathway 2

TS (**b2**) ZPE=0.163678 E_{B,0K}=-1113.862528 E_{m,0K}=-1113.244301 E_{C,0K}=-1110.221036

W	2.058081	1.027290	0.025085
W	0.605028	-2.030704	0.104355
W	-1.600459	0.288973	-0.393560
O	2.763598	1.699184	-1.385441
O	3.042397	1.375626	1.383447
O	2.076869	-0.917957	-0.306726
O	0.093128	0.425717	0.366465
O	0.532844	-2.295938	1.797005
O	0.941268	-3.541718	-0.621161

O	-1.764336	0.695727	-2.035289
O	-1.202292	-1.544492	-0.510321
O	-3.204316	0.267399	0.510266
O	-1.449839	2.404746	0.027393
C	-0.611261	3.002860	0.775052
H	0.999789	2.490408	0.230852
H	-0.310283	2.530665	1.715759
C	-0.410673	4.480609	0.626089
H	-1.236592	4.974415	1.157076
H	0.529253	4.795972	1.081025
H	-0.451492	4.775385	-0.423456
C	-4.616142	0.581914	0.476401
C	-5.412202	-0.563164	1.086483
H	-4.901585	0.765321	-0.563709
H	-4.740738	1.506627	1.048472
H	-6.476117	-0.305346	1.073020
H	-5.271657	-1.484072	0.514902
H	-5.109597	-0.740364	2.121640

W₃O₈(OC₂H₅)(H)•CH₃CH=O (c2)

ZPE=0.163678 E_{B,0K}=-1113.877726 E_{m,0K}=-1113.257311 E_{C,0K}=-1110.231703

W	1.338901	2.035984	0.199130
W	1.720910	-1.648337	-0.012050
W	-1.555693	-0.551062	-0.534253
O	2.789185	2.914338	-0.033344
O	0.725058	2.498223	1.728487
O	2.002093	0.184219	0.024100
O	-0.512575	0.893455	-0.392595
O	2.041322	-2.362874	1.516865
O	2.686909	-2.415232	-1.206376
O	-2.162745	-0.773825	-2.115914
O	-0.144052	-1.794470	-0.427424
O	-2.589042	-1.194224	0.864002
O	-3.205514	1.055903	-0.390187
C	-3.022535	2.279415	-0.434601
H	0.476973	3.052755	-0.891221
H	-1.991630	2.655810	-0.511853
C	-4.139034	3.261548	-0.384414
H	-3.973767	3.937520	0.463912
H	-4.094859	3.886701	-1.285113
H	-5.109623	2.771835	-0.305716
C	-3.892759	-1.578676	1.340069
C	-3.840523	-1.843174	2.838380
H	-4.199396	-2.472158	0.786700

H	-4.583366	-0.764060	1.098772
H	-4.835171	-2.136769	3.189675
H	-3.140125	-2.650803	3.066014
H	-3.529835	-0.946886	3.382062

W₃O₈(OC₂H₅) (H) (d2)

ZPE=0.105557 E_{B,0K}=-960.0013929 E_{m,0K}=-959.4782368 E_{C,0K}=-956.7351142

W	-1.911219	-1.541839	0.027599
W	-0.723144	1.979744	0.172203
W	1.792213	-0.273698	-0.578793
O	-3.606910	-1.725900	-0.000722
O	-1.368874	-2.294989	1.460777
O	-1.684535	0.412177	-0.079965
O	0.366281	-1.285920	-0.684789
O	-0.848875	2.551792	1.782880
O	-1.231980	3.213866	-0.901869
O	2.588942	-0.272340	-2.089462
O	1.095273	1.424736	-0.192273
O	2.926806	-0.862254	0.739673
H	-1.629548	-2.697926	-1.207021
C	4.199674	-1.471347	1.076994
C	4.838450	-0.721195	2.236169
H	4.828938	-1.451887	0.182043
H	3.981506	-2.509741	1.341412
H	5.783872	-1.207771	2.496263
H	5.048367	0.317063	1.965258
H	4.188210	-0.735138	3.114421

Pathway 3

TS (b3) ZPE=0.164703 E_{B,0K}=-1113.854647 E_{m,0K}=-1113.232351

W	1.642710	-1.565320	-0.451329
W	1.387001	1.735596	0.467792
W	-1.724379	-0.156959	-0.080486
O	2.190591	-2.769808	0.640718
O	2.078270	-2.018105	-2.048381
O	2.346164	0.139472	-0.019006
O	-0.227523	-1.349722	-0.309716
O	1.928815	3.133905	-0.373026
O	1.504290	2.003440	2.161514
O	-2.195243	0.133857	1.670409
O	-0.343779	1.300668	-0.026070
O	-2.684265	0.835239	-1.283153
O	-2.970130	-1.537490	0.158636

C	-3.527243	-2.075110	1.251169
H	-2.911039	-0.597754	1.974072
H	-4.615642	-2.146138	1.196808
C	-2.785545	-3.168190	1.977830
H	-3.241549	-3.328545	2.959014
H	-2.840325	-4.117587	1.425686
H	-1.728796	-2.921712	2.116759
C	-2.726254	2.111416	-1.965831
C	-3.842844	2.978270	-1.402977
H	-2.883385	1.886649	-3.024646
H	-1.745270	2.579670	-1.838339
H	-3.867386	3.927547	-1.948040
H	-4.814253	2.488909	-1.515424
H	-3.673185	3.193592	-0.344762

$\text{W}_3\text{O}_7(\text{OC}_2\text{H}_5)(\text{OH})\cdot\text{CH}_3\text{CH}=\text{O}$ (c3)

ZPE=0.166779 $E_{\text{B},0\text{K}}=-1113.86483$ $E_{\text{m},0\text{K}}=-1113.245105$

W	1.657240	-1.455581	-0.516590
W	1.254789	1.785297	0.404667
W	-1.736953	-0.154518	0.003101
O	2.174435	-2.542363	0.715839
O	2.157179	-2.030422	-2.058620
O	2.328511	0.300627	-0.174538
O	-0.198456	-1.251976	-0.443590
O	1.777245	3.300028	-0.225159
O	1.215588	1.816475	2.134240
O	-1.777375	0.203913	1.871444
O	-0.443962	1.351159	-0.174316
O	-2.875112	0.473878	-1.268870
O	-2.712310	-1.783195	0.443333
C	-2.850635	-2.851648	1.108894
H	-1.223151	0.937935	2.195505
H	-3.704738	-3.477245	0.838484
C	-1.921722	-3.276771	2.198592
H	-2.471691	-3.377170	3.143225
H	-1.503416	-4.265234	1.968727
H	-1.109748	-2.562455	2.335942
C	-3.586011	1.469830	-2.031133
C	-3.582676	2.821808	-1.329948
H	-4.601433	1.085862	-2.167140
H	-3.094973	1.520208	-3.007220
H	-4.125674	3.545342	-1.946228
H	-4.078574	2.759249	-0.356891
H	-2.561915	3.184553	-1.188110

W₃O₇(OC₂H₅) (OH) (d3)

ZPE=0.105557 E_{B,0K}=-930.001393 E_{m,0K}=-959.478237

W	0.550428	1.997879	-0.085023
W	2.005586	-1.106964	0.135701
W	-1.648168	-0.931340	-0.139806
O	0.576705	2.832556	-1.582804
O	0.524612	3.144551	1.189945
O	2.025296	0.799442	0.060871
O	-0.938958	0.859429	0.022913
O	2.532264	-1.669645	1.667685
O	2.986142	-1.809781	-1.083420
O	-2.166670	-2.591779	-0.785753
O	0.198707	-1.520980	-0.146986
O	-3.302213	-0.359482	0.328080
H	-1.759186	-3.268991	-1.340548
C	-4.296260	0.381259	1.045759
C	-5.536163	0.576065	0.181933
H	-3.845114	1.338269	1.328566
H	-4.523285	-0.185579	1.953949
H	-6.282436	1.141308	0.748963
H	-5.293550	1.134933	-0.725565
H	-5.969583	-0.386883	-0.100244

Pathway 4

TS (b4) ZPE=0.164003 E_{B,0K}=-1113.83894 E_{m,0K}=-1113.218458

W	-2.143789	-0.768940	-0.126855
W	-0.362841	2.181801	0.209752
W	1.497577	-0.836503	-0.455271
O	-3.507854	-1.009524	-1.122292
O	-2.249474	-1.868483	1.366780
O	-1.941691	1.039391	0.314847
O	-0.660937	-1.119283	-1.007288
O	0.114028	2.623527	1.799337
O	-0.611119	3.593670	-0.731684
O	1.998424	-1.673273	-1.850474
O	0.887080	1.049786	-0.565317
O	3.130476	-0.247301	0.313569
O	1.070185	-1.952298	0.955728
C	0.531596	-2.887554	1.739506
H	-1.399168	-2.331054	1.643557
H	0.444719	-2.564224	2.779162
C	0.824036	-4.324612	1.415310
H	0.252260	-4.978976	2.079480
H	0.554986	-4.564466	0.380541

H	1.891227	-4.564256	1.541446
C	4.053232	0.695100	-0.264795
C	5.091260	1.095998	0.776247
H	3.502371	1.575256	-0.621994
H	4.531684	0.217830	-1.130348
H	5.802701	1.803937	0.337772
H	4.612069	1.572681	1.636081
H	5.643337	0.219461	1.126737

W₃O₇(OC₂H₅)(OH)·CH₃CH=O (c4)

ZPE=0.164642 E_{B,0K}=-1113.856961 E_{m,0K}=-1113.235035

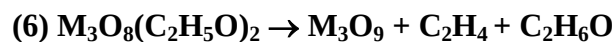
W	1.643007	1.619622	-0.023595
W	1.454557	-1.771934	0.201837
W	-1.638695	0.001447	-0.563575
O	2.279283	2.414000	-1.389634
O	1.841364	2.621259	1.567314
O	2.440465	-0.045490	0.175504
O	-0.108582	1.281496	-0.307524
O	1.226173	-2.206366	1.854634
O	2.287564	-3.009517	-0.658014
O	-2.201618	-0.033294	-2.165209
O	-0.127424	-1.284375	-0.595411
O	-2.465992	-1.260559	0.624847
O	-2.778092	1.427939	0.212618
C	-3.070681	2.094902	1.251609
H	2.481647	3.332643	1.712207
H	-2.603881	1.818976	2.201992
C	-4.036999	3.230663	1.194366
H	-4.898942	3.032972	1.846068
H	-3.569914	4.152593	1.564909
H	-4.387666	3.387083	0.172651
C	-3.829662	-1.434867	1.022583
C	-4.420290	-2.679947	0.363133
H	-4.427974	-0.552123	0.759451
H	-3.841897	-1.542669	2.114759
H	-5.450388	-2.834061	0.704019
H	-4.426890	-2.573427	-0.725792
H	-3.829779	-3.563298	0.621307

W₃O₇(OC₂H₅)(OH) (d4)

ZPE=0.10738 E_{B,0K}=-959.975083 E_{m,0K}=-959.454098

W	-1.864335	-1.051603	0.280519
W	-0.478313	1.906824	-0.148177
W	1.661484	-0.886581	-0.568752

O	-2.894942	-1.782984	-0.858225
O	-2.066401	-1.787606	2.014252
O	-2.040344	0.816896	0.294007
O	-0.126982	-1.473913	-0.161197
O	0.262624	2.360807	1.345621
O	-0.877824	3.268930	-1.119001
O	2.254742	-1.676003	-1.953528
O	0.686895	0.728542	-1.012229
O	2.894399	-0.646951	0.785612
H	-1.415958	-2.297348	2.521527
C	3.224368	-0.044202	2.059276
C	4.561806	0.676208	1.961892
H	3.265926	-0.860985	2.787137
H	2.421141	0.646060	2.338040
H	4.811407	1.107951	2.936580
H	5.356870	-0.015740	1.671518
H	4.512368	1.486913	1.230058



For M=Mo (Figure S12a)

TS (b) ZPE=0.162482 $E_{\text{B},0\text{K}}=-1115.288264$ $E_{\text{m},0\text{K}}=-1114.630069$ $E_{\text{C},0\text{K}}=-1111.748945$

MO	-2.430315	-1.208193	-0.022527
MO	-1.141558	1.983445	0.241756
MO	1.236513	-0.797709	-0.346386
O	-3.266992	-1.777287	-1.386271
O	-3.053717	-1.986783	1.352879
O	-2.533318	0.686015	0.127319
O	-0.588851	-1.471207	-0.170924
O	-0.977392	2.572078	1.829977
O	-1.385915	3.301030	-0.804678
O	1.613059	-1.315181	-1.911015
O	0.347320	0.993308	-0.253170
O	2.856639	0.365821	-0.107644
O	1.936125	-1.890820	0.831966
C	3.861920	-2.222182	1.438857
H	3.457912	-2.320124	2.440159
H	3.845434	-3.118999	0.829116
C	4.657801	-1.116480	1.083206
H	5.384597	-1.281633	0.287755
H	3.818049	-0.345862	0.492531
H	4.988549	-0.476392	1.900671
C	4.352115	2.291462	-0.340060
C	3.304631	1.409207	-1.006165

H	5.257120	1.730030	-0.088896
H	4.636092	3.094085	-1.028037
H	3.953181	2.745413	0.571141
H	2.419443	1.994776	-1.269660
H	3.690282	0.934069	-1.916728

Mo₃O₉·C₂H₆O·C₂H₄ (c)

ZPE=0.166187 E_{B,0K}=-1115.334374 E_{m,0K}=-1114.678397 E_{C,0K}=-1111.80323

MO	-2.506086	-1.264569	-0.063171
MO	-1.229655	1.969325	0.186498
MO	1.119880	-0.837169	-0.091551
O	-3.241792	-1.827096	-1.483012
O	-3.265824	-2.011766	1.254997
O	-2.580049	0.631228	0.059949
O	-0.652825	-1.579364	-0.065589
O	-1.287773	2.780277	1.676327
O	-1.350685	3.124024	-1.052478
O	1.750089	-1.385593	-1.569322
O	0.339386	0.970968	0.014240
O	2.923288	0.504950	0.062953
O	1.887843	-1.661527	1.181342
C	5.253253	-1.779767	0.049770
H	4.442220	-2.417834	-0.292511
H	6.024451	-1.527836	-0.674885
C	5.313399	-1.346556	1.318985
H	6.134859	-0.726015	1.670025
H	3.716440	-0.038712	0.268262
H	4.550938	-1.621096	2.043609
C	4.354572	2.417285	-0.509706
C	3.256053	1.475809	-0.979788
H	5.286190	1.879368	-0.307838
H	4.555780	3.154981	-1.293003
H	4.050630	2.948134	0.396192
H	2.327475	2.013433	-1.171085
H	3.540254	0.927493	-1.884183

Mo₃O₉·C₂H₄ (d2) ZPE=0.084463 E_{B,0K}=-960.2427339 E_{m,0K}=-959.6947411 E_{C,0K}=-957.1028871

MO	-2.072363	-1.031077	0.000065
MO	-0.396271	2.035212	-0.000039
MO	1.559568	-1.047369	-0.000258
O	-2.901578	-1.583967	-1.368671
O	-2.899497	-1.583035	1.370445

O	-1.896260	0.860921	-0.000561
O	-0.268200	-1.589807	-0.001020
O	-0.370313	3.030056	1.372927
O	-0.368993	3.029262	-1.373560
O	2.224917	-1.775189	-1.379651
O	1.057377	0.847788	0.000984
O	2.224567	-1.777199	1.378254
C	3.980757	0.381082	-0.674151
H	4.537443	-0.360032	-1.239464
H	3.461867	1.150139	-1.239424
C	3.980430	0.380249	0.676222
H	3.461340	1.148682	1.242160
H	4.536832	-0.361584	1.240881

For M=W (Figure S13a)

TS (b) ZPE=0.162232 $E_{B,0K}=-1113.864615$ $E_{m,0K}=-1113.238671$ $E_{C,0K}=-1110.215986$

W	-2.161010	-1.285546	0.000314
W	-1.022295	1.967359	0.156481
W	1.496680	-0.749503	-0.244951
O	-2.899282	-1.935873	-1.405328
O	-2.830590	-2.049853	1.383704
O	-2.359477	0.609273	0.074696
O	-0.304599	-1.489934	-0.043136
O	-0.977061	2.705299	1.707961
O	-1.245678	3.183344	-1.036648
O	1.871548	-1.275623	-1.825721
O	0.543727	1.013480	-0.155378
O	3.077330	0.460208	-0.034581
O	2.256628	-1.824440	0.924329
C	4.293454	-2.103892	1.405144
H	3.938407	-2.251537	2.418712
H	4.247328	-2.968313	0.751751
C	5.012134	-0.953626	1.045217
H	5.681015	-1.043898	0.189427
H	4.077435	-0.226076	0.544974
H	5.361672	-0.320255	1.859911
C	4.489794	2.450288	-0.269920
C	3.492056	1.516989	-0.941148
H	5.415066	1.932146	-0.001332
H	4.747174	3.258056	-0.962224
H	4.059134	2.895261	0.631156
H	2.587966	2.061500	-1.224796
H	3.910017	1.046536	-1.838989

$W_3O_9 \cdot C_2H_6O \cdot C_2H_4$ (c)

ZPE=0.166097 E_{B,0K}=-1113.903682 E_{m,0K}=-1113.278925 E_{C,0K}=-1110.262059

W	-2.235152	-1.277824	-0.032793
W	-1.014421	1.972916	0.127196
W	1.394304	-0.809078	-0.079460
O	-2.963260	-1.896722	-1.454729
O	-2.981490	-2.006276	1.326427
O	-2.357214	0.622129	0.038289
O	-0.377996	-1.565429	-0.028555
O	-1.111957	2.871250	1.585057
O	-1.107118	3.059661	-1.197722
O	1.978286	-1.360318	-1.593997
O	0.577131	0.993016	0.050906
O	3.144154	0.522609	0.065505
O	2.176812	-1.678933	1.178582
C	5.533993	-1.643563	0.092654
H	4.764825	-2.316313	-0.278865
H	6.312655	-1.345972	-0.606349
C	5.538078	-1.226491	1.369241
H	6.319196	-0.573322	1.751985
H	3.945135	-0.004206	0.297263
H	4.769918	-1.549973	2.067154
C	4.542519	2.469726	-0.476441
C	3.482506	1.501963	-0.976625
H	5.480933	1.956171	-0.246030
H	4.747065	3.208895	-1.257265
H	4.198643	2.996782	0.417131
H	2.546598	2.014791	-1.196327
H	3.803607	0.950304	-1.865493

W₃O₉•C₂H₄ (d2)

ZPE=0.084647 E_{B,0K}=-958.8070106 E_{m,0K}=-958.290881 E_{C,0K}=-955.5570737

W	-1.873614	-1.184361	0.000013
W	-0.493122	2.010353	-0.000032
W	1.764955	-0.890516	-0.000127
O	-2.646647	-1.819145	-1.388896
O	-2.644252	-1.818175	1.390703
O	-1.896144	0.719107	-0.000578
O	-0.025678	-1.566424	-0.001299
O	-0.543576	3.008036	1.393029
O	-0.542245	3.007256	-1.393700
O	2.454485	-1.608544	-1.395717
O	1.060334	0.956143	0.000950
O	2.453371	-1.609402	1.395540
C	3.942064	0.658201	-0.676748

H	4.567417	-0.026292	-1.240723
H	3.369202	1.388406	-1.241593
C	3.941707	0.658334	0.678084
H	3.368532	1.388674	1.242422
H	4.566856	-0.026002	1.242490



For M=Mo (Figure S12b)

TS (f) ZPE=0.164011 $E_{\text{B},0\text{K}}=-1115.303738$ $E_{\text{m},0\text{K}}=-1114.651969$ $E_{\text{C},0\text{K}}=-1111.770002$

MO	-2.034230	-1.549027	0.308377
MO	-1.404582	1.796446	-0.029948
MO	1.337917	-0.494008	-0.758500
O	-2.913056	-2.513980	-0.777779
O	-2.254522	-2.153246	1.882421
O	-2.544127	0.284948	0.191218
O	-0.218589	-1.478557	-0.122205
O	-1.008456	2.471127	1.487854
O	-2.086661	3.001514	-1.015405
O	1.623059	-0.829081	-2.369799
O	0.129330	1.080251	-0.783533
O	2.705143	0.813152	-0.084816
O	2.618670	-1.552262	0.168703
C	3.551274	-1.238080	1.082184
H	3.437462	0.172758	0.563874
H	3.158690	-1.072012	2.092759
C	4.882986	-1.932635	0.968185
H	4.811698	-2.979948	1.290710
H	5.245501	-1.920592	-0.063503
H	5.617111	-1.436404	1.610335
C	2.675831	2.718125	1.485719
C	2.845772	2.261298	0.044802
H	3.420059	2.255589	2.142034
H	2.817069	3.802812	1.532114
H	1.673094	2.492924	1.857194
H	2.082059	2.687728	-0.607001
H	3.833355	2.510684	-0.354162



ZPE=0.167984 $E_{\text{B},0\text{K}}=-1115.327886$ $E_{\text{m},0\text{K}}=-1114.679343$ $E_{\text{C},0\text{K}}=-1111.789779$

MO	-0.915717	-2.051737	0.207380
MO	-2.142463	1.083861	0.053202
MO	1.367160	0.404527	-0.884817

O	-1.392456	-3.602034	-0.315383
O	-0.154807	-2.124993	1.751593
O	-2.361446	-0.793934	0.293223
O	0.258516	-1.258783	-0.954113
O	-2.506171	1.938803	1.486600
O	-3.118162	1.678299	-1.209058
O	1.880557	0.749385	-2.434169
O	-0.335475	1.273707	-0.331993
O	2.212959	2.005816	0.315533
O	2.762131	-0.781252	-0.040421
C	2.950256	-1.609951	0.889348
H	3.152099	1.958573	0.549015
H	2.168022	-1.744298	1.645389
C	4.200528	-2.417742	0.964761
H	3.940363	-3.483880	0.942084
H	4.874011	-2.185569	0.138285
H	4.705286	-2.244055	1.923719
C	1.997283	3.867732	1.917503
C	1.716732	3.384013	0.505588
H	3.072007	3.903412	2.131133
H	1.605435	4.883343	2.030248
H	1.505435	3.229116	2.655564
H	0.651354	3.310839	0.299136
H	2.194895	4.008780	-0.254385

Mo₃O₈•CH₃CH=O (h1)

ZPE=0.085121 E_{B,0K}=-960.223634 E_{m,0K}=-959.6784877 E_{C,0K}=-957.0724835

MO	-0.059645	1.901739	-0.358136
MO	2.210941	-0.590809	0.414920
MO	-1.121949	-1.410860	-0.585461
O	-0.145489	3.318511	-1.293042
O	-0.679448	2.165588	1.221247
O	1.696603	1.127403	-0.168709
O	-0.936186	0.477389	-1.142334
O	2.586408	-0.595663	2.070807
O	3.551890	-1.169101	-0.447341
O	-1.839013	-2.380117	-1.747561
O	0.655763	-1.651685	0.089149
O	-2.595729	-0.810199	0.619883
C	-3.016188	-0.046418	1.523737
H	-2.299684	0.594437	2.048739
C	-4.457512	-0.006432	1.895355
H	-4.822073	1.025729	1.821304

H	-5.052077	-0.661102	1.256783
H	-4.574924	-0.301895	2.946255

Mo₃O₈•C₂H₅OH (**h2**)

ZPE=0.109988 E_{B,0K}=-961.4272653 E_{m,0K}=-960.8793421 E_{C,0K}=-958.2741173

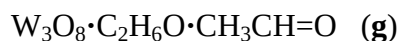
MO	-2.324095	-0.314181	0.386298
MO	0.306753	1.844190	-0.420217
MO	0.872069	-1.642811	-0.455879
O	-3.710313	-0.681952	-0.520828
O	-2.752606	-0.241945	2.028318
O	-1.524080	1.297146	-0.185490
O	-0.958344	-1.615105	0.122667
O	0.967963	2.240962	1.110723
O	0.568494	3.119350	-1.515192
O	1.525951	-2.763323	-1.516137
O	1.050278	0.264145	-1.014430
O	2.446795	-1.179731	0.901233
H	2.617984	-1.790156	1.632985
C	3.873253	0.508862	2.001840
C	3.613030	-0.274090	0.728534
H	4.114901	-0.153209	2.841218
H	4.734959	1.164820	1.841537
H	3.011200	1.128992	2.256955
H	3.334933	0.367197	-0.104884
H	4.456685	-0.905006	0.434522

For M=W (Figure S13b)

TS (f) ZPE=0.165582 E_{B,0K}=-1113.859793 E_{m,0K}=-1113.238683 E_{C,0K}=-1110.213979

W	-1.800759	-1.576977	0.236565
W	-1.275625	1.786639	-0.009783
W	1.596169	-0.399440	-0.646817
O	-2.664565	-2.596848	-0.840763
O	-1.971485	-2.160592	1.844619
O	-2.385256	0.241283	0.115881
O	0.004641	-1.452259	-0.212403
O	-0.993604	2.453687	1.554588
O	-1.928355	2.994211	-1.042728
O	2.011669	-0.672298	-2.262532
O	0.341832	1.137439	-0.655094
O	2.923281	0.940903	0.135100
O	2.814508	-1.431071	0.352686
C	3.709763	-1.289671	1.332715
H	3.601077	0.411072	0.747930

H	3.283284	-1.119510	2.325120
C	4.989671	-2.069645	1.224111
H	4.833174	-3.134333	1.450218
H	5.411495	-2.000652	0.216963
H	5.720973	-1.684320	1.941126
C	2.768367	2.867036	1.677361
C	3.033435	2.403632	0.254646
H	3.480686	2.426173	2.381976
H	2.886758	3.954534	1.718852
H	1.749184	2.627128	1.990596
H	2.301758	2.800107	-0.448136
H	4.038726	2.659651	-0.089850



ZPE=0.167828 $E_{\text{B},0\text{K}}=-1113.86412$ $E_{\text{m},0\text{K}}=-1113.245513$ $E_{\text{C},0\text{K}}=-1110.217396$

W	0.323337	2.103473	0.138348
W	2.144454	-0.720817	-0.012234
W	-1.485423	-0.793174	-0.704630
O	0.410272	3.730499	-0.416950
O	-0.285907	2.019477	1.759703
O	2.010364	1.179779	0.097091
O	-0.753249	1.044728	-0.918983
O	2.522573	-1.387956	1.535984
O	3.315451	-1.231121	-1.163681
O	-2.113727	-1.291010	-2.193070
O	0.434587	-1.271193	-0.482156
O	-1.755593	-2.436062	0.630182
O	-2.944986	0.056319	0.261610
C	-3.365518	0.805473	1.205477
H	-2.553822	-2.458534	1.181342
H	-2.648180	1.128205	1.963005
C	-4.787006	1.257068	1.245508
H	-4.830658	2.353359	1.200911
H	-5.352137	0.843877	0.407652
H	-5.264118	0.964670	2.189885
C	-0.353678	-3.585637	2.321016
C	-0.908475	-3.627179	0.909228
H	-1.152806	-3.571646	3.070561
H	0.242753	-4.488112	2.489211
H	0.299874	-2.721775	2.462584
H	-0.124652	-3.579171	0.156884
H	-1.541751	-4.498609	0.722874



ZPE=0.084918 E_{B,0K}=-958.7548159 E_{m,0K}=-958.2394123 E_{C,0K}=-955.4918028

W	-0.255304	1.925149	-0.252771
W	2.160967	-0.535218	0.296271
W	-1.182911	-1.435604	-0.389258
O	-0.452464	3.342253	-1.202228
O	-0.768212	2.193377	1.376249
O	1.518556	1.173152	-0.200685
O	-1.143218	0.452719	-0.962337
O	2.711669	-0.537264	1.918649
O	3.438071	-1.045511	-0.723966
O	-1.878656	-2.545048	-1.465294
O	0.632068	-1.675828	0.126223
O	-2.653353	-0.840339	0.749632
C	-3.194098	-0.050841	1.580670
H	-2.553077	0.652251	2.118134
C	-4.654476	-0.121266	1.865008
H	-5.097205	0.878574	1.781431
H	-5.157991	-0.807800	1.182380
H	-4.819673	-0.450631	2.900131

W₃O₈·C₂H₆O (h2)

ZPE=0.109933 E_{B,0K}=-959.9756487 E_{m,0K}=-959.4620692 E_{C,0K}=-956.7203985

W	-1.922540	-0.121738	0.368067
W	0.782711	1.677499	-0.065923
W	0.622531	-1.245652	-0.821046
O	-3.258684	-0.056526	-0.700273
O	-2.493556	-0.350021	1.971867
O	-1.073145	1.597185	0.381307
O	-0.955391	-1.795743	0.028553
O	1.563469	2.200055	1.373533
O	0.986918	2.861731	-1.286085
O	0.300736	-1.297224	-2.485375
O	1.867362	0.117302	-0.567298
O	1.570212	-2.233767	0.959019
H	0.974821	-2.738225	1.538696
C	2.784565	-1.357493	2.930455
C	2.900227	-2.057714	1.587128
H	2.175391	-1.933534	3.635235
H	3.785807	-1.258634	3.361854
H	2.361203	-0.356140	2.821618
H	3.462751	-1.462533	0.868412
H	3.347967	-3.051688	1.665465